(51) International Patent Classification[7]:   D06M 13/46, 15/277, 15/576, 15/333, C09K 3/16

(21) International Application Number: PCT/US00/25097

(22) International Filing Date:
13 September 2000 (13.09.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/474,711   29 December 1999 (29.12.1999)   US

(71) Applicant: 3M INNOVATIVE PROPERTIES COMPANY [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(72) Inventors: THOMPSON, Delton, R.; Post Office Box 33427, Saint Paul, MN 55133-3427 (US). KLUN, Thomas, P.; Post Office Box 33427, Saint Paul, MN 55133-3427 (US). LAMANNA, William, M.; Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(74) Agents: WEISS, Lucy, C. et al.; Office of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AT (utility model), AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, CZ (utility model), DE, DE (utility model), DK, DK (utility model), DM, DZ, EE, EE (utility model), ES, FI, FI (utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KR (utility model), KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— With international search report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: WATER- AND OIL-REPELLENT, ANTISTATIC COMPOSITION

(57) Abstract: A water- and oil-repellent, antistatic composition comprises (a) at least one nonpolymeric ionic salt consisting of (i) at least one cation selected from the group consisting of monovalent metal cations, divalent metal cations, and organic onium cations, and (ii) at least one weakly coordinating anion, the conjugate acid of the anion having an acidity greater than or equal to that of a hydrocarbon sulfonic acid, and with the proviso that the anion is organic or fluoroorganic when the cation is a metal; (b) at least one fluorochemical repellency-imparting additive or repellent; and (c) at least one insulating material. The composition exhibits good antistatic and repellency characteristics.

WATER- AND OIL-REPELLENT, ANTISTATIC COMPOSITION

Field of the Invention

This invention relates to compositions that exhibit both repellency and
5   antistatic characteristics. This invention further relates to fibers, films, fabrics,
coatings, and molded or blown articles comprising the compositions. In other
aspects, this invention also relates to a topical treatment composition and to
processes for imparting both repellency and antistatic characteristics to substrates.

Background of the Invention

10   Various fluorochemicals have been used to impart water and oil repellency,
as well as soil resistance, to a variety of substrates (for example, textiles, carpet,
leather, paper, and non-woven webs). These fluorochemicals have most often been
applied topically (for example, by spraying, padding, or finish bath immersion), but
15   some fluorochemicals have also been useful as polymer melt additives for
preparing water- and oil-repellent polymeric fibers, films, fabrics, etc. The
resulting repellent substrates have found use in numerous applications where water
and/or oil repellency (as well as soil resistance) characteristics have been valued.

For some applications, however, antistatic properties have also been
20   necessary or desirable.

Electrostatic charge buildup is responsible for a variety of problems in the
processing and use of many industrial products and materials. Electrostatic
charging can cause materials to stick together or to repel one another. This is a
particular problem in fiber and textile processing. In addition, static charge buildup
25   can cause objects to attract dirt and dust, thereby decreasing the effectiveness of
fluorochemical repellents.

Sudden electrostatic discharges from insulating objects can also be a
serious problem. With photographic film, such discharges can cause fogging and
the appearance of artifacts. When flammable materials are present (for example, in
30   a surgical environment), a static electric discharge can serve as an ignition source,
resulting in fires and/or explosions. Static is a particular problem in the electronics

industry, since modern electronic devices are extremely susceptible to permanent damage by static electric discharges.

However, conventional antistats (many of which are humectants that rely on the adsorption and conductivity of water for charge dissipation) have generally not

5   been very effective in combination with fluorochemical repellents. The result of such combination has often been a substantial deterioration (or even elimination) of either antistatic or repellency characteristics (or both), relative to the use of either additive alone.

Furthermore, it has been particularly difficult to combine conventional

10   antistats and fluorochemical repellents in polymer melt processing applications, as, for example, the water associated with humectant antistats vaporizes rapidly at melt processing temperatures. This has resulted in the undesirable formation of bubbles in the polymer and has caused screw slippage in extrusion equipment. Many antistats have also lacked the requisite thermal stability, leading to the

15   production of objectionable odors (for example, in melt blowing applications, where high extrusion temperatures are involved).

Thus, there remains a need in the art for antistatic agents and repellents that can be effectively combined to impart both good antistatic characteristics and good repellency characteristics to substrates and that, in particular, can be utilized as

20   melt additives without causing processing problems or melt defects.

Summary of the Invention

Briefly, in one aspect, this invention provides a water- and oil-repellent, antistatic composition comprising (a) at least one nonpolymeric ionic salt

25   consisting of (i) at least one monovalent metal cation, divalent metal cation, or organic onium cation (for example, a quaternary ammonium ion) and (ii) at least one weakly coordinating anion, the conjugate acid of the anion having an acidity greater than or equal to that of a hydrocarbon sulfonic acid (for example, a bis(perfluoroalkanesulfonyl)imide ion), and with the proviso that the anion is

30   organic or fluoroorganic when the cation is a metal; (b) at least one fluorochemical repellency-imparting additive or repellent; and (c) at least one insulating material. As used herein, the term "organic onium cation" means a positively charged

organic ion having at least part of its charge localized on at least one heteroatom (for example, nitrogen, phosphorus, sulfur, iodine, or oxygen). Preferably, the insulating material is a thermoplastic or thermosetting polymer (more preferably, thermoplastic), and the composition is prepared by forming a blend (more

5   preferably, a melt blend) of the components.

It has been discovered that the above-described class of ionic salt antistatic agents or antistats can be effectively combined with fluorochemical repellents to impart both good antistatic characteristics and good repellency characteristics to a variety of insulating materials. The antistats and repellents can be combined not

10   only in topical treatments (external additives) but even (and preferably) as melt additives (internal additives) without causing processing problems or melt defects. The antistat/repellent combination used in the composition of the invention is surprisingly effective at dissipating the static charge that can accumulate in an otherwise insulating substrate such as a polymer film or fabric, while also

15   imparting durable water and oil repellency (and soil resistance). Even more suprisingly, when used in topical treatments or as polymer melt additives in polypropylene melt-blown nonwoven fabric, certain preferred antistats exhibit synergistic behavior when combined with the repellent(s), in that better static dissipation rates are obtained than when the antistats are used alone.

20   The combination of ionic salt antistat(s) and fluorochemical repellent(s) used in the composition of the invention is compatible with a variety of polymers. Since many of the antistats are hydrophobic (immiscible with water), the antistatic performance of the combination is often relatively independent of atmospheric humidity levels and durable even under exposure to aqueous environments. In

25   addition, since many of the antistats are stable at temperatures up to 300-500°C, the combination of such antistat(s) with thermally stable fluorochemical repellent(s) is particularly well-suited for use in high temperature polymer melt additive applications and in applications where the use temperatures are very high.

The combination of ionic salt antistat(s) and fluorochemical repellent(s)

30   used in the composition of the invention therefore meets the need in the art for antistatic agents and repellents that can be effectively combined to impart both good antistatic characteristics and good repellency characteristics to substrates and

that, in particular, can be utilized as melt additives without causing processing problems or melt defects.

In other aspects, this invention also provides fiber, fabric, film, a coating, and a molded or blown article comprising the composition of the invention;

5   processes for imparting both repellency and antistatic characteristics to a substrate, for example, by bulk addition or by topical treatment; and a topical treatment composition comprising (a) at least one nonpolymeric ionic salt consisting of (i) at least one monovalent metal cation, divalent metal cation, or organic onium cation and (ii) at least one weakly coordinating anion, the conjugate acid of the anion

10   having an acidity greater than or equal to that of a hydrocarbon sulfonic acid, and with the proviso that the anion is organic or fluoroorganic when the cation is a metal, and (b) at least one fluorochemical repellency-imparting additive or repellent.

15   **Detailed Description of the Invention**

Antistats

Ionic salts suitable for use as antistats in the composition of the invention are those that consist of a monovalent or divalent metal cation (preferably,

20   monovalent) or an organic onium cation (preferably, an organic onium cation) and a weakly coordinating anion. Suitable metal cations include, for example, lithium, calcium, sodium, potassium, magnesium, zinc, iron, nickel, and copper, with sodium and lithium being preferred. The organic onium cation can comprise a heteroatom (for example, nitrogen, phosphorus, sulfur, iodine, or oxygen;

25   preferably, nitrogen or phosphorus; more preferably, nitrogen) as the charge center or as a component element in a charge-delocalized chain or ring structure. The organic onium cation can be cyclic (that is, where the charge center(s) of the cation are ring atoms) or acyclic (that is, where the charge center(s) of the cation are not ring atoms but can have cyclic substituents). The cyclic cations can be aromatic,

30   unsaturated but nonaromatic, or saturated, and the acyclic cations can be saturated or unsaturated.
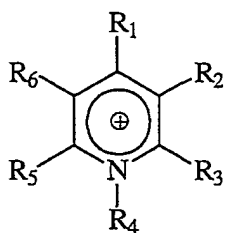
The cyclic cations can contain one or more ring heteroatoms (for example, nitrogen, oxygen, or sulfur), and the ring atoms can bear substituents (for example, hydrogen, halogen, or organic groups such as alkyl, alicyclic, aryl, alkalicyclic, alkaryl, alicyclicalkyl, aralkyl, aralicyclic, and alicyclicaryl groups). Separate alkyl substituents can be joined together to constitute a unitary alkylene radical of from 2 to 4 carbon atoms forming a ring structure. Organic substituents can contain one or more heteroatoms such as, for example, nitrogen, oxygen, sulfur, phosphorus, or halogen (and thus can be fluoroorganic in nature).

The acyclic cations can have at least one (preferably, at least two; more preferably, at least three; most preferably, four) charge center-bonded organic substituents or R groups, with the remaining substituents being hydrogen. The R groups can be cyclic or acyclic, saturated or unsaturated, aromatic or nonaromatic, and can contain one or more heteroatoms such as, for example, nitrogen, oxygen, sulfur, phosphorus, or halogen (and thus can be fluoroorganic in nature).
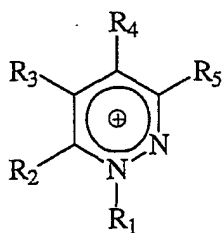
Preferably, the organic onium cation is acyclic or unsaturated cyclic. More preferably, it is acyclic or aromatic, most preferably, acyclic.

Preferred acyclic organic onium cations are nitrogen onium (ammonium) and phosphorus onium (phosphonium) cations that are quaternary or tertiary (most preferably, quaternary) cations. The quaternary and tertiary cations are preferably of low symmetry (having at least two, preferably at least three, different charge center-bonded organic substituents or R groups as defined above) and more preferably contain at least one hydroxyl group in at least one charge center-bonded organic substituent. Most preferred acyclic organic onium cations are the nitrogen onium cations described below for the ionic salt antistats of Formula I.
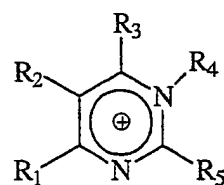
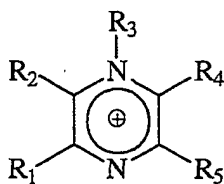Preferred aromatic organic onium cations are the nitrogen onium cations selected from the group consisting of

R_1
R_6 R_2
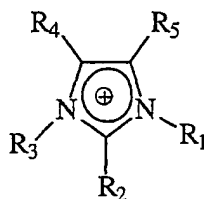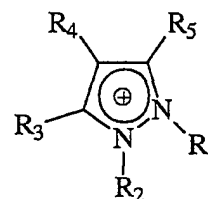⊕
R_5 R_3
N
R_4

Pyridinium

R_4
R_3 R_5
⊕
R_2 N
N
R_1

Pyridazinium

R_3
R_2 N–R_4
⊕
R_1 N
R_5

Pyrimidinium

,   ,   ,

R_3
N
R_2 R_4
⊕
R_1 N
R_5

Pyrazinium

R_4 R_5
N ⊕ N
R_3 R_1
R_2

Imidazolium

R_4 R_5
⊕
R_3 N
N R_1
R_2

Pyrazolium

,   ,

R_4 R_1
N
⊕
R_3 R_2
S

Thiazolium

R_4 R_1
N
⊕
R_3 R_2
O

Oxazolium

, and

R_1
N–N
⊕
R_4 R_2
N
R_3
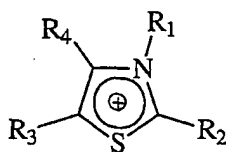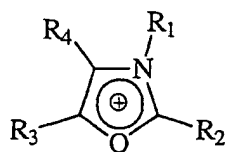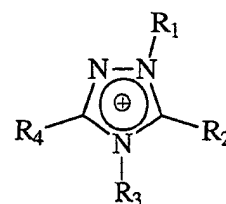
Triazolium

wherein R_1, R_2, R_3, R_4, R_5, and R_6 are independently selected from the group
consisting of H, F, alkyl groups of from 1 to about 18 carbon atoms (preferably,
from 1 to about 11 carbon atoms), two said alkyl groups joined together to form a
unitary alkylene radical of from 2 to 4 carbon atoms forming a ring structure, and
phenyl groups; and wherein said alkyl groups, alkylene radicals, or phenyl groups
can comprise one or more substituent groups (preferably, a group that is capable of
hydrogen bonding, for example, an amino, hydroxyl, acetyl, or acetamide group, or
an electron-withdrawing group, for example, F-, Cl-, CF_3-, SF_5-, CF_3S-,
$(CF_3)_2CHS$-, and $(CF_3)_3 CS$-).

Preferred unsaturated cyclic, nonaromatic organic onium cations include the
nitrogen onium cations represented by the following formula

$$
\begin{array}{c}
R_1 \\
R_7-N \overset{\oplus}{=} N-R_2 \\
R_6 \quad R_5 \quad R_4 \quad R_3
\end{array}
$$
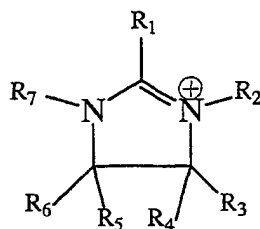
5   where R_1, R_2, R_3, R_4, R_5, R_6, and R_7 are defined as R_1, R_2, R_3, R_4, R_5, and R_6 are
defined above for the preferred aromatic organic onium cations.

Suitable weakly coordinating anions have a conjugate acid that is at least as
acidic as a hydrocarbon sulfonic acid (preferably, a hydrocarbon sulfonic acid
having from 1 to about 20 carbon atoms; more preferably, an alkane, aryl, or

10   alkaryl sulfonic acid having from 1 to about 8 carbon atoms; even more preferably,
methane or p-toluene sulfonic acid; most preferably, p-toluene sulfonic acid).
Preferably, the conjugate acid is a strong acid. More preferably, the Hammett
acidity function, H_0, of the neat conjugate acid of the anion is less than about -7
(most preferably, less than about -10).

15   Representative examples of suitable weakly coordinating anions include
BF_4^-; PF_6^-; SbF_6^-; AsF_6^-; ClO_4^-; NO_3^-; Cl^-; Br^-; F^-; HSO_4^-; $H_2PO_4^-$; organic
anions such as alkane, aryl, and alkaryl sulfonates; fluorinated and unfluorinated
tetraarylborates; carboranes and halogen-, alkyl-, or haloakyl-substituted carborane
anions including metallocarborane anions; teflates (for example, $^-OTeF_5$, $^-$

20    $B(OTeF_5)_4$, and $^-Pd(OTeF_5)_4$); and fluoroorganic anions such as
perfluoroalkanesulfonates, cyanoperfluoroalkanesulfonylamides,
bis(cyano)perfluoroalkanesulfonylmethides, bis(perfluoroalkanesulfonyl)imides,
bis(perfluoroalkanesulfonyl)methides, and tris(perfluoroalkanesulfonyl)methides;
and the like. Preferred anions include organic and fluoroorganic anions (more

25   preferably, alkane, aryl, and alkaryl sulfonates, as well as
perfluoroalkanesulfonates, bis(perfluoroalkanesulfonyl)imides, and

tris(perfluoroalkanesulfonyl)methides; most preferably, alkane sulfonates, perfluoroalkanesulfonates, and bis(perfluoroalkanesulfonyl)imides).

The fluoroorganic anions can be either fully fluorinated, that is perfluorinated, or partially fluorinated (within the organic portion thereof).

5   Preferred fluoroorganic anions include those that comprise at least one highly fluorinated alkanesulfonyl group, that is, a perfluoroalkanesulfonyl group or a partially fluorinated alkanesulfonyl group wherein all non-fluorine carbon-bonded substituents are bonded to carbon atoms other than the carbon atom that is directly bonded to the sulfonyl group (preferably, all non-fluorine carbon-bonded

10   substituents are bonded to carbon atoms that are more than two carbon atoms away from the sulfonyl group).

Preferably, the fluoroorganic anion is at least about 80 percent fluorinated (that is, at least about 80 percent of the carbon-bonded substituents of the anion are fluorine atoms). More preferably, the anion is perfluorinated (that is, fully

15   fluorinated, where all of the carbon-bonded substituents are fluorine atoms). The anions, including the preferred perfluorinated anions, can contain one or more catenary (that is, in-chain) heteroatoms such as, for example, nitrogen, oxygen, or sulfur.

Preferred fluoroorganic anions include perfluoroalkanesulfonates,

20   bis(perfluoroalkanesulfonyl)imides, and tris(perfluoroalkanesulfonyl)methides. The perfluoroalkanesulfonates and bis(perfluoroalkanesulfonyl)imides are more preferred anions, with the perfluoroalkanesulfonates being most preferred.

The ionic salt antistats can be solids or liquids under use conditions but preferably have melting points less than about 150°C (more preferably, less than

25   about 50°C; most preferably, less than about 25°C). Liquid ionic salts are preferred due to their generally better static dissipative performance. For use as polymer melt additives, the ionic salt antistats are preferably stable at temperatures of about 250°C and above (more preferably, about 300°C and above) and are preferably miscible with the insulating material at the melt processing temperature. (In other

30   words, the onset of decomposition of the antistats is above such temperatures.) Preferred ionic salt antistats for polymer melt additive applications include those having cations selected from the group consisting of alkyl phosphonium cations,

aromatic nitrogen onium cations (preferably, the preferred aromatic organic onium cations set forth above), and acyclic nitrogen onium cations (preferably, the cations shown in Formula I below); and having organic or fluoroorganic anions (preferably, anions selected from the group consisting of alkane sulfonates, aryl

5 sulfonates, alkaryl sulfonates, perfluoroalkanesulfonates, bis(perfluoroalkanesulfonyl)imides, and tris(perfluoroalkanesulfonyl)methides; more preferably, alkane sulfonates, perfluoroalkanesulfonates, and bis(perfluoroalkanesulfonyl)imides); most preferably, perfluoroalkanesulfonates and bis(perfluoroalkanesulfonyl)imides.

10 The antistats are also preferably hydrophobic. Thus, a preferred class of ionic salt antistats for use in the composition of the invention includes those that consist of (a) an aromatic nitrogen onium cation selected from the group consisting of
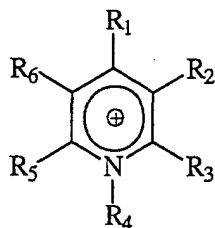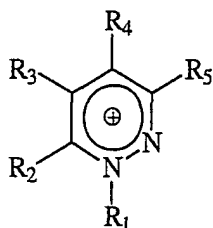
Pyridinium   Pyridazinium   Pyrimidinium
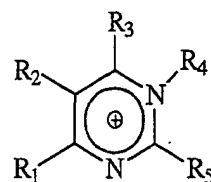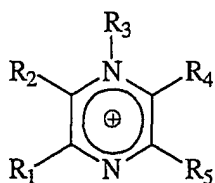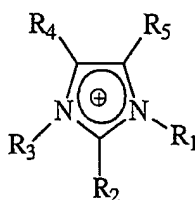
Pyrazinium   Imidazolium   Pyrazolium
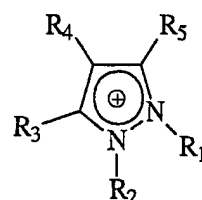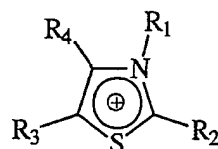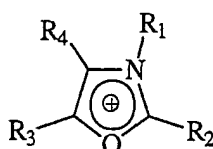
Thiazolium   Oxazolium   Triazolium

wherein R_1, R_2, R_3, R_4, R_5, and R_6 are independently selected from the group consisting of H, F, alkyl groups of from 1 to about 18 carbon atoms (preferably, from 1 to about 11 carbon atoms), two said alkyl groups joined together to form a

5   unitary alkylene radical of from 2 to 4 carbon atoms forming a ring structure, and phenyl groups; and wherein said alkyl groups, alkylene radicals, or phenyl groups can comprise one or more substituent groups (preferably, an electron-withdrawing group, for example, F-, Cl-, CF_3-, SF_5-, CF_3S-, $(CF_3)_2CHS$-, and $(CF_3)_3 CS$-); and

(b) a weakly coordinating fluoroorganic anion in accordance with the above

10   description or a weakly coordinating anion selected from the group consisting of BF_4-, PF_6-, AsF_6-, and SbF_6-. This preferred class comprises a most preferred

subclass of the hydrophobic ionic liquids described in U.S. Pat. No. 5,827,602
(Koch et al.).

Another preferred class of ionic salt antistats useful in preparing the
composition of the invention is the class of compounds represented by Formula I
5   below

$$(R_1)_{4-z}N^+[(CH_2)_qOR_2]_z \, X^- \qquad (I)$$
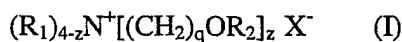
wherein each R_1 is independently selected from the group consisting of alkyl,
10   alicyclic, aryl, alkalicyclic, alkaryl, alicyclicalkyl, aralkyl, aralicyclic, and
alicyclicaryl moieties that can contain one or more heteroatoms such as, for
example, nitrogen, oxygen, sulfur, phosphorus, or halogen (and thus can be
fluoroorganic in nature); each R_2 is independently selected from the group
consisting of hydrogen and the moieties described above for R_1; z is an integer of 1
15   to 4; q is an integer of 1 to 4; and X^- is a weakly coordinating alkane sulfonate, aryl
sulfonate, alkaryl sulfonate, or fluoroorganic anion as described above (preferably,
a fluoroorganic anion). R_1 is preferably alkyl, and R_2 is preferably selected from
the group consisting of hydrogen, alkyl, and acyl (more preferably, hydrogen or
acyl; most preferably, hydrogen). Most preferably, z is 1, q is 2, R_1 is alkyl, and R_2
20   is hydrogen.

Many of the above-described ionic salt antistats (for example, metal
bis(perfluoroalkanesulfonyl)imides, metal perfluoroalkanesulfonates, onium
halides, onium alkanesulfonates, onium arylsulfonates, onium tetrafluoroborates,
and onium hexafluorophosphates) are commercially available and can also be
25   prepared by standard methods known in the art. Other ionic salt antistats
comprising an organic onium cation can be prepared by ion exchange or metathesis
reactions, which are also well known in the art. For example, a precursor onium
salt can be combined with a precursor metal salt or the corresponding acid of a
weakly coordinating anion in aqueous solution. Upon combining, the desired
30   product (the onium salt of the weakly coordinating anion) precipitates (as a liquid
or solid) or can be preferentially extracted into an organic solvent (for example,
methylene chloride). The product can be isolated by filtration or by liquid/liquid

phase separation, can be washed with water to completely remove byproduct metal salt or acid (if present), and can then be dried thoroughly under vacuum to remove all volatiles (including water and organic solvent, if present). Similar metathesis reactions can be conducted in organic solvents (for example, acetonitrile) rather

5   than in water, and, in this case, the salt byproduct generally preferentially precipitates, while the desired product salt remains dissolved in the organic solvent (from which it can be isolated using standard experimental techniques).

Weakly coordinating fluoroorganic anions (for use in preparing such ionic salts) can be prepared by standard methods known in the art, and metal salts of

10   many are commercially available. Such methods include the anion precursor preparative methods described in the following references: imide precursors - U.S. Patent Nos. 5,874,616 (Howells et al.), 5,723,664 (Sakaguchi et al.), 5,072,040 (Armand), and 4,387,222 (Koshar); methide precursors - U.S. Patent Nos. 5,554,664 (Lamanna et al.) and 5,273,840 (Dominey); sulfonate precursors - U.S.

15   Patent Nos. 5,176,943 (Wou), 4,582,781 (Chen et al.), 3,476,753 (Hanson), and 2,732,398 (Brice et al.); sulfonate, imide, and methide precursors having caternary oxygen or nitrogen in a fluorochemical group - U.S. Patent No. 5,514,493 (Waddell et al.); disulfone precursors - R.J. Koshar and R.A. Mitsch, J. Org. Chem., 38, 3358 (1973) and U.S. Patent No. 5,136,097 (Armand).

20   In general, cyano-containing methides and amides containing fluoroalkanesulfonyl groups can be prepared by the reaction of fluoroalkanesulfonyl fluorides, R_fSO_2F, with anhydrous malononitrile or cyanamide, respectively, in the presence of a non-nucleophilic base. This synthetic procedure is described in Scheme 1 of U.S. Patent No. 5,874,616 (Howells et al.)

25   for the preparation of bis(fluoroalkanesulfonyl)imides and involves the substitution of either malononitrile or cyanamide for the fluoroalkanesulfonamide. The resulting intermediate non-nucleophilic base cation-containing methide or amide salt can be converted to the desired cation salt (typically lithium) via standard metathesis reactions well known in the art.

30   Representative examples of useful ionic salt antistats include octyldimethyl-2-hydroxyethylammonium bis(trifluoromethylsulfonyl)imide:
[$C_8H_{17}N^+(CH_3)_2CH_2CH_2OH$ $^-N(SO_2CF_3)_2$],

-12-
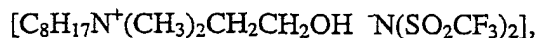
octyldimethyl-2-hydroxyethylammonium perfluorobutanesulfonate:

$[C_8H_{17}N^+(CH_3)_2CH_2CH_2OH \; ^-OSO_2C_4F_9]$;

octyldimethyl-2-hydroxyethylammonium trifluoromethanesulfonate:

$[C_8H_{17}N^+(CH_3)_2CH_2CH_2OH \; ^-OSO_2CF_3]$,

5 octyldimethyl-2-hydroxyethylammonium tris(trifluoromethanesulfonyl)methide:

$[C_8H_{17}N^+(CH_3)_2CH_2CH_2OH \; ^-C(SO_2CF_3)_3]$,

trimethyl-2-acetoxyethylammonium bis(trifluoromethylsulfonyl)imide:

$[(CH_3)_3N^+CH_2CH_2OC(O)CH3 \; ^-N(SO_2CF_3)_2]$,

trimethyl-2-hydroxyethylammonium bis(perfluorobutanesulfonyl)imide:

10 $[(CH_3)_3N^+CH_2CH_2OH \; ^-N(SO_2C_4F_9)_2]$,

triethylammonium bis(perfluoroethanesulfonyl)imide: $[Et_3N^+H \; ^-N(SO_2C_2F_5)_2]$,

tetraethylammonium trifluoromethanesulfonate:

$[CF_3SO_3^- \; ^+NEt_4]$,

tetraethylammonium bis(trifluoromethanesulfonyl)imide: $[(CF_3SO_2)_2N^- \; ^+NEt_4]$,

15 tetramethylammonium tris(trifluoromethanesulfonyl)methide:

$[(CH_3)_4N^+ \; ^-C(SO_2CF_3)_3]$,

tetrabutylammonium bis(trifluoromethanesulfonyl)imide:

$[(C_4H_9)_4N^+ \; ^-N(SO_2CF_3)_2]$,

trimethyl-3-perfluorooctylsulfonamidopropylammonium

20 bis(trifluoromethanesulfonyl)imide:

$[C_8F_{17}SO_2NH(CH_2)_3N^+(CH_3)_3 \; ^-N(SO_2CF_3)_2]$,

1-hexadecylpyridinium bis(perfluoroethanesulfonyl)imide:

$[n\text{-}C_{16}H_{33}\text{-}cyc\text{-}N^+C_5H_5 \; ^-N(SO_2C_2F_5)_2]$,

1-hexadecylpyridinium perfluorobutanesulfonate:

25 $[n\text{-}C_{16}H_{33}\text{-}cyc\text{-}N^+C_5H_5 \; ^-OSO_2C_4F_9]$,

1-hexadecylpyridinium perfluorooctanesulfonate:

$[n\text{-}C_{16}H_{33}\text{-}cyc\text{-}N^+C_5H_5 \; ^-OSO_2C_8F_{17}]$,

n-butylpyridinium bis(trifluoromethanesulfonyl)imide:

$[n\text{-}C_4H_9\text{-}cyc\text{-}N^+C_5H_5 \; ^-N(SO_2CF_3)_2]$,

30 n-butylpyridinium perfluorobutanesulfonate:

$[n\text{-}C_4H_9\text{-}cyc\text{-}N^+C_5H_5 \; ^-OSO_2C_4F_9]$,

1,3-ethylmethylimidazolium bis(trifluoromethanesulfonyl)imide:

$[CH_3\text{-}cyc\text{-}(N^+C_2H_2NCH)CH_2CH_3\ ^-N(SO_2CF_3)_2]$,

1,3-ethylmethylimidazolium nonafluorobutanesulfonate:

$[CH_3\text{-}cyc\text{-}(N^+C_2H_2NCH)CH_2CH_3\ ^-OSO_2C_4F_9]$,

1,3-ethylmethylimidazolium trifluoromethanesulfonate: $[CH_3\text{-}cyc\text{-}$

5 $(N^+C_2H_2NCH)CH_2CH_3\ ^-OSO_2CF_3]$,

1,3-ethylmethylimidazolium hexafluorophosphate:

$[CH_3\text{-}cyc\text{-}(N^+C_2H_2NCH)CH_2CH_3\ PF_6^-]$,

1,3-ethylmethylimidazolium tetrafluoroborate:

$[CH_3\text{-}cyc\text{-}(N^+C_2H_2NCH)CH_2CH_3\ BF_4^-]$,

10 lithium perfluorobutanesulfonate: $[Li^+\ ^-OSO_2C_4F_9]$,

lithium trifluoromethanesulfonate: $[Li^+\ ^-OSO_2CF_3]$,

lithium bis(trifluoromethanesulfonyl)imide: $[Li^+\ ^-N(SO_2CF_3)_2]$,

lithium tris(trifluoromethanesulfonyl)methide: $[Li^+\ ^-C(SO_2CF_3)_3]$,

sodium phenylbis(trifluoromethanesulfonyl)methide: $[Na^+\ ^-C(C_6H_5)(SO_2CF_3)_2]$,

15 octyldimethyl-2-hydroxyethylammonium teflate: $[C_8H_{17}N^+(CH_3)_2CH_2CH_2OH\ ^-$

$OTeF_5]$,

lithium permethylmonocarba-closo-dodecaborate: $[Li^+\ ^-CB_{11}(CH_3)_{12}]$,

sodium monocarba-closo-dodecaborate: $[Na^+\ ^-CB_{11}H_{12}]$,

sodium tetrakis-(pentafluorophenyl)borate:

20 $[Na^+\ ^-B(C_6F_5)_4]$,

octyldimethyl-2-hydroxyethylammonium methanesulfonate:

$[C_8H_{17}N^+(CH_3)_2CH_2CH_2OH\ ^-OSO_2CH_3]$,

tetrabutylphosphonium perfluorobutanesulfonate: $[(C_4H_9)_4P^+\ ^-OSO_2C_4F_9]$,

tetraphenylphosphonium bis(trifluoromethanesulfonyl)imide: $[(C_6H_5)_4P^+\ ^-$

25 $N(SO_2CF_3)_2]$,

trioctylmethylammonium chloride: $[(C_8H_{17})_3(CH_3)N^+\ Cl^-]$,

trioctylmethylammonium trifluoromethanesulfonate: $[(C_8H_{17})_3(CH_3)N^+\ ^-$

$OSO_2CF_3]$,

trioctylmethylammonium perfluorobutanesulfonate: $[(C_8H_{17})_3(CH_3)N^+\ ^-$

30 $OSO_2C_4F_9]$,

3-(2-hydroxyethyl)-1-methyl-2-undecylimidazolinium p-toluenesulfonate:

$[CH_3\text{-}cyc\text{-}(N^+C_2H_4N(CH_2CH_2OH)C)C_{11}H_{23}\ ^-OSO_2C_6H_4CH_3]$,

1-dodecyl-2-ethyl-3-(2-hydroxyethyl)imidazolinium p-toluenesulfonate:

$[C_{12}H_{25}\text{-}cyc\text{-}(N^+C_2H_4N(CH_2CH_2OH)C)C_2H_5 \ ^-OSO_2C_6H_4CH_3]$,

1,2-dimethyl-3-propylimidazolium bis(trifluoromethanesulfonyl)imide,

1,2-dimethyl-3-propylimidazolium tris(trifluoromethanesulfonyl)methide,

5   1,2-dimethyl-3-propylimidazolium trifluoromethanesulfonyl

perfluorobutanesulfonylimide,

1-ethyl-3-methylimidazolium cyanotrifluoromethanesulfonylamide,

1-ethyl-3-methylimidazolium bis(cyano)trifluoromethanesulfonylmethide,

1-ethyl-3-methylimidazolium

10   trifluoromethanesulfonylperfluorobutanesulfonylimide,

octyldimethyl-2-hydroxyethylammonium

trifluoromethylsulfonylperfluorobutanesulfonylimide,

2-hydroxyethyltrimethylammonium

trifluoromethylsulfonylperfluorobutanesulfonylimide,

15   2-methoxyethyltrimethylammonium bis(trifluoromethanesulfonyl)imide

octyldimethyl-2-hydroxyethylammonium

bis(cyano)trifluoromethanesulfonylmethide,

trimethyl-2-acetoxyethylammonium

trifluoromethylsulfonylperfluorobutanesulfonylimide,

20   1-butylpyridinium trifluoromethylsulfonylperfluorobutanesulfonylimide,

2-ethoxyethyltrimethylammonium trifluoromethanesulfonate,

1-butyl-3-methylimidazolium perfluorobutanesulfonate,

perfluoro-1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide,

1-ethyl-2-methylpyrazolium perfluorobutanesulfonate,

25   1-butyl-2-ethylpyrazolium trifluoromethanesulfonate,

N-ethylthiazolium bis(trifluoromethanesulfonyl)imide,

N-ethyloxazolium bis(trifluoromethanesulfonyl)imide, and 1-butylpyrimidinium

perfluorobutanesulfonylbis(trifluoromethanesulfonyl)-methide, 1,3-

ethylmethylimidazolium hexafluorophosphate, 1,3-ethylmethylimidazolium

30   tetrafluoroborate, and mixtures thereof.

     Preferred ionic salt antistats include octyldimethyl-2-

hydroxyethylammonium bis(trifluoromethylsulfonyl)imide:

$[C_8H_{17}N^+(CH_3)_2CH_2CH_2OH\ \ ^-N(SO_2CF_3)_2]$,

octyldimethyl-2-hydroxyethylammonium perfluorobutanesulfonate:

$[C_8H_{17}N^+(CH_3)_2CH_2CH_2OH\ \ ^-OSO_2C_4F_9]$,

octyldimethyl-2-hydroxyethylammonium trifluoromethanesulfonate:

5      $[C_8H_{17}N^+(CH_3)_2CH_2CH_2OH\ \ ^-OSO_2CF_3]$,

octyldimethyl-2-hydroxyethylammonium tris(trifluoromethanesulfonyl)methide:

$[C_8H_{17}N^+(CH_3)_2CH_2CH_2OH\ \ ^-C(SO_2CF_3)_3]$,

trimethyl-2-acetoxyethylammonium bis(trifluoromethylsulfonyl)imide:

$[(CH_3)_3N^+CH_2CH_2OC(O)CH3\ \ ^-N(SO_2CF_3)_2]$,

10   trimethyl-2-hydroxyethylammonium bis(perfluorobutanesulfonyl)imide:

$[(CH_3)_3N^+CH_2CH_2OH\ \ ^-N(SO_2C_4F_9)_2]$,

triethylammonium bis(perfluoroethanesulfonyl)imide: $[Et_3N^+H\ \ ^-N(SO_2C_2F_5)_2]$,

tetraethylammonium trifluoromethanesulfonate:

$[CF_3SO_3^-\ ^+NEt_4]$,

15   tetraethylammonium bis(trifluoromethanesulfonyl)imide: $[(CF_3SO_2)_2N^-\ ^+NEt_4]$,

tetramethylammonium tris(trifluoromethanesulfonyl)methide:

$[(CH_3)_4N^+\ \ ^-C(SO_2CF_3)_3]$,

tetrabutylammonium bis(trifluoromethanesulfonyl)imide:

$[(C_4H_9)_4N^+\ \ ^-N(SO_2CF_3)_2]$,

20   trimethyl-3-perfluorooctylsulfonamidopropylammonium

bis(trifluoromethanesulfonyl)imide:

$[C_8F_{17}SO_2NH(CH_2)_3N^+(CH_3)_3\ \ ^-N(SO_2CF_3)_2]$,

1-hexadecylpyridinium bis(perfluoroethanesulfonyl)imide:

$[n\text{-}C_{16}H_{33}\text{-}cyc\text{-}N^+C_5H_5\ \ ^-N(SO_2C_2F_5)_2]$,

25   1-hexadecylpyridinium perfluorobutanesulfonate:

$[n\text{-}C_{16}H_{33}\text{-}cyc\text{-}N^+C_5H_5\ \ ^-OSO_2C_4F_9]$,

1-hexadecylpyridinium perfluorooctanesulfonate:

$[n\text{-}C_{16}H_{33}\text{-}cyc\text{-}N^+C_5H_5\ \ ^-OSO_2C_8F_{17}]$,

n-butylpyridinium bis(trifluoromethanesulfonyl)imide:

30     $[n\text{-}C_4H_9\text{-}cyc\text{-}N^+C_5H_5\ \ ^-N(SO_2CF_3)_2]$,

n-butylpyridinium perfluorobutanesulfonate:

$[n\text{-}C_4H_9\text{-}cyc\text{-}N^+C_5H_5\ \ ^-OSO_2C_4F_9]$,

1,3-ethylmethylimidazolium bis(trifluoromethanesulfonyl)imide:

[CH_3-cyc-($N^+C_2H_2NCH$)CH_2CH_3 $^-N(SO_2CF3)_2$],

1,3-ethylmethylimidazolium nonafluorobutanesulfonate:

[CH_3-cyc-($N^+C_2H_2NCH$)CH_2CH_3 $^-OSO_2C_4F_9$],

5   1,3-ethylmethylimidazolium trifluoromethanesulfonate: [CH_3-cyc-

($N^+C_2H_2NCH$)CH_2CH_3 $^-OSO_2CF_3$],

lithium perfluorobutanesulfonate: [Li^+ $^-OSO_2C_4F_9$],

lithium trifluoromethanesulfonate: [Li^+ $^-OSO_2CF_3$],

lithium bis(trifluoromethanesulfonyl)imide: [Li^+ $^-N(SO_2CF_3)_2$],

10   tetrabutylphosphonium perfluorobutanesulfonate: [$(C_4H_9)_4P^+$ $^-OSO_2C_4F_9$],

octyldimethyl-2-hydroxyethylammonium methanesulfonate:

[$C_8H_{17}N^+(CH_3)_2CH_2CH_2OH$ $^-OSO_2CH_3$],

1-dodecyl-2-ethyl-3-(2-hydroxyethyl)imidazolinium p-toluenesulfonate:

[$C_{12}H_{25}$-cyc-($N^+C_2H_4N(CH_2CH_2OH)C$)C_2H_5 $^-OSO_2C_6H_4CH_3$],

15   1,3-ethylmethylimidazolium tetrafluoroborate, and mixtures thereof.

More preferred ionic salt antistats include octyldimethyl-2-

hydroxyethylammonium bis(trifluoromethylsulfonyl)imide, octyldimethyl-2-

hydroxyethylammonium perfluorobutanesulfonate, octyldimethyl-2-

hydroxyethylammonium trifluoromethanesulfonate, triethylammonium

20   bis(perfluoroethanesulfonyl)imide, tetraethylammonium trifluoromethanesulfonate,

trimethyl-3-perfluorooctylsulfonamidopropylammonium

bis(trifluoromethanesulfonyl)imide, 1,3-ethylmethylimidazolium

nonafluorobutanesulfonate, 1,3-ethylmethylimidazolium

bis(trifluoromethanesulfonyl)imide, 1,3-ethylmethylimidazolium

25   trifluoromethanesulfonate, tetrabutylphosphonium perfluorobutanesulfonate, and

mixtures thereof.

More preferred ionic salt antistats include octyldimethyl-2-

hydroxyethylammonium bis (trifluoromethylsulfonyl)imide, octyldimethyl-2-

hydroxyethylammonium trifluoromethanesulfonate, octyldimethyl-2-

30   hydroxyethylammonium nonafluorobutanesulfonate, triethylammonium

bis(perfluoroethanesulfonyl)imide, 1,3-ethylmethylimidazolium

nonafluorobutanesulfonate, 1,3-ethylmethylimidazolium

bis(trifluoromethanesulfonyl)imide, 1,3-ethylmethylimidazolium trifluoromethanesulfonate, tetrabutylphosphonium perfluorobutanesulfonate, and mixtures thereof, with further preferences being in accordance with the general cation and anion preferences set forth above.

5

Fluorochemical Repellents

Suitable fluorochemical repellency-imparting additives or repellents for use in the composition of the invention are those that comprise at least one fluorochemical group, preferably, at least one fluoroaliphatic or fluoroalicyclic

10   group. Such fluorochemicals include any of the fluorochemical group-containing polymeric and oligomeric compounds known in the art to impart water and oil repellency to substrates. These polymeric and oligomeric fluorochemicals typically comprise one or more fluorochemical groups that contain a perfluorinated carbon chain having from 3 to about 20 carbon atoms, more preferably from about 4 to

15   about 12 carbon atoms. These fluorochemical groups can contain straight chain, branched chain, or cyclic fluorinated alkylene groups or any combination thereof. The fluorochemical groups can optionally contain catenary (i.e., in-chain) heteroatoms such as oxygen, divalent or hexavalent sulfur, or nitrogen. Fully-fluorinated groups are preferred, but hydrogen or chlorine atoms can also be

20   present as substituents, provided that no more than one atom of either is present for every two carbon atoms. It is additionally preferred that any fluorochemical group contain at least about 40% fluorine by weight, more preferably at least about 50% fluorine by weight. The terminal portion of the group is generally fully-fluorinated, preferably containing at least 7 fluorine atoms, e.g., $CF_3CF_2CF_2-$, $(CF_3)_2CF-$,

25   SF_5CF_2-. Perfluorinated aliphatic groups (i.e., those of the formula $C_nF_{2n+1}-$) are the most preferred fluorochemical groups.

Representative examples of suitable fluorochemicals include fluorochemical urethanes, ureas and substituted ureas, esters, ethers, alcohols, epoxides, allophanates, amides, amines (and salts thereof), acids (and salts thereof),

30   carbodiimides, guanidines, oxazolidinones, isocyanurates, piperazines,

aminoalcohols, sulfones, imides, biurets, acrylate and methacrylate homopolymers and copolymers, siloxanes, alkoxysilanes, chlorosilanes, and mixtures thereof.

Representative fluorochemical group-containing polymers useful in the present invention include fluorochemical acrylate and methacrylate homopolymers

5   or copolymers containing fluorochemical acrylate monomers interpolymerized with monomers such as methyl methacrylate, butyl acrylate, octadecylmethacrylate, acrylate and methacrylate esters of oxyalkylene and polyoxyalkylene polyol oligomers (e.g., oxyethylene glycol dimethacrylate, polyoxyethylene glycol dimethacrylate, methoxy acrylate, and polyoxyethylene acrylate), glycidyl

10 methacrylate, ethylene, butadiene, styrene, isoprene, chloroprene, vinyl acetate, vinyl chloride, vinylidene chloride, vinylidene fluoride, acrylonitrile, vinyl chloroacetate, vinylpyridine, vinyl alkyl ethers, vinyl alkyl ketones, acrylic acid, methacrylic acid, 2-hydroxyethylacrylate, N-methylolacrylamide, 2-(N,N,N-trimethylammonium)ethyl methacrylate, and 2-acrylamido-2-

15 methylpropanesulfonic acid (AMPS). The relative amounts of various comonomers used can generally be selected empirically, depending on the substrate to be treated, the properties desired, and the mode of application to the substrate. Useful fluorochemicals also include blends of the various fluorochemicals described above.

20   Also useful in the present invention are blends of fluorochemicals with fluorine-free extender compounds, such as siloxanes, (meth)acrylate and substituted acrylate polymers and copolymers, N-methylolacrylamide-containing acrylate polymers, urethanes, blocked isocyanate-containing polymers and oligomers, condensates or precondensates of urea or melamine with formaldehyde,

25 glyoxal resins, condensates of fatty acids with melamine or urea derivatives, condensates of fatty acids with polyamides and their epichlorohydrin adducts, waxes, polyethylene, chlorinated polyethylene, alkyl ketene dimers, esters, and amides. Blends of these fluorine-free extender compounds can also be used. The relative amount of extender compound to fluorochemical is not critical. However,

30 the overall composition of the fluorochemical treatment generally contains, relative to the amount of solids present in the system, at least about 3 weight percent,

preferably at least about 5 weight percent, carbon-bound fluorine in the form of said fluorochemical groups.

Many fluorochemicals, including blends that include fluorine-free extender molecules such as those described above, are commercially available as ready-

5   made formulations. Such products are sold, for example, as Scotchgard™ brand Carpet Protector (manufactured by 3M Co., Saint Paul, Minnesota) and as Zonyl™ brand Carpet Treatment (manufactured by E.I. du Pont de Nemours and Company, Wilmington, Delaware).

Useful fluorochemicals are described in European Patent No. 0 613 462

10   (Minnesota Mining and Manufacturing Company) and in U.S. Patent Nos. 3,728,151 (Sherman et al.), 3,816,229 (Bierbrauer), 3,896,035 (Schultz et al.), 3,901,727 (Loudas), 3,916,053 (Sherman et al.), 4,043,923 (Loudas), 4,043,964 (Sherman et al.), 4,264,484 (Patel), 4,624,889 (Bries), 5,274,159 (Pellerite et al.), 5,380,778 (Buckanin), and 5,451,622 (Boardman et al.).

15   Fluorochemical repellents suitable for use as polymer melt additives are preferably stable at temperatures of 250°C and above (more preferably, 300°C and above), are preferably miscible with the insulating material at the melt processing temperature, and are preferably capable of migration to the surface of the insulating material. Thus, a preferred class of fluorochemical repellents, useful both in

20   topical treatments and as polymer melt (or other bulk polymer) additives, includes fluorochemical oxazolidinone compositions or fluorochemical oxazolidinones comprising normally solid, water-insoluble, fluoroaliphatic radical-containing 2-oxazolidinone compounds, the compounds comprising one or more 2-oxazolidinone moieties,

$$
\begin{array}{c}
O \\
\parallel \\
C \\
\diagup \quad \diagdown \\
{-}N \qquad O \\
\mid \qquad \mid \\
CH_2{-}CH{-}
\end{array}
$$
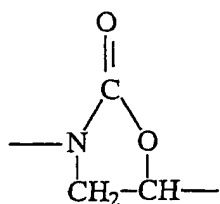
25   ,

at least one of which has a monovalent fluoroaliphatic radical, R_f, bonded to the 5-position carbon atom thereof by an organic linking group.

A preferred subclass of such fluoroaliphatic radical-containing oxazolidinone compounds is that represented by Formula II below:

$$
\left[\begin{array}{c} \underset{\text{R}^1-\text{CH}-\text{CH}_2}{\overset{\overset{\displaystyle O}{\underset{\displaystyle C}{\|}}}{\underset{\displaystyle}{O}\diagdown\underset{\displaystyle}{N}}}-\text{A} \end{array}\right]\left[\begin{array}{c} \text{N}-\underset{\underset{\text{CH}_2-\text{CH}-\text{R}^2}{}}{\overset{\overset{\displaystyle O}{\underset{\displaystyle C}{\|}}}{\overset{\displaystyle}{O}}} \end{array}\right]_a \left[\begin{array}{c} \underset{-\text{CH}-\text{CH}_2}{\overset{\overset{\displaystyle O}{\underset{\displaystyle C}{\|}}}{\underset{\displaystyle}{O}\diagdown\underset{\displaystyle}{N}}}-\text{A} \end{array}\right]\left[\begin{array}{c} \text{N}-\underset{\underset{\text{CH}_2-\text{CH}-\text{R}^1}{}}{\overset{\overset{\displaystyle O}{\underset{\displaystyle C}{\|}}}{\overset{\displaystyle}{O}}} \end{array}\right]_b \quad (\text{II})
$$
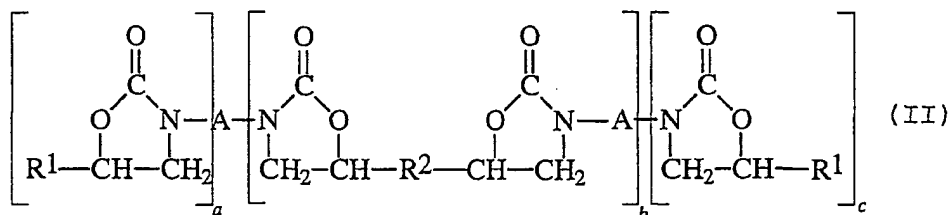
where each R^1 is independently hydrogen or an organic radical, which organic radical can contain $-Q-R_f$ where Q is a linking group and R_f is a fluoroaliphatic radical that can optionally contain one or more catenary (in-chain) heteroatoms such as oxygen; each R^2 is independently an organic radical, which organic radical can contain $-Q-R_f$ where Q and R_f are as defined above; with the proviso that there is at least one R_f radical in one of R^1 and R^2; each A is independently an organic radical; a is zero or 1; b is a number from 0 to about 6; c is 0, 1, or 2; and the sum of a+b+c is at least 1. Preferably, R_1 is an organic radical that contains $-QR_f$, where R_f is a perfluoroalkyl group having from about 3 to about 20 carbon atoms (preferably, from about 4 to about 12 carbon atoms), and Q comprises a heteroatom-containing group, an organic group, or a combination thereof (preferably, Q is $-SO_2N(R')(CH_2)_k-$, $-(CH_2)_k-$, $-CON(R')(CH_2)_k-$, or $-(CH_2)_kSO_2N(R')(CH_2)_k-$, where R' is hydrogen, phenyl, or a short chain (up to about 6 carbon atoms) alkyl group (preferably, methyl or ethyl), and each k is independently an integer from 1 to about 20); a is 1; b is 0; c is 0; and A is an alkyl group having from about 12 to about 22 carbon atoms. Formula II represents individual compounds or mixtures of compounds, for example, as they are obtained as products from reactions used in their preparation.

Such fluorochemical oxazolidinone compositions can be prepared using known organic reactions, for example, by the reaction of epoxides or halohydrins (for example, chlorohydrins or bromohydrins) with organic isocyanates in each which reaction at least one of the reactants contains an R_f radical. The reactions

can be carried out stepwise by reacting the halohydrin with the isocyanate under urethane bond-forming conditions, for example, 20°C to 100°C for about 1 to 24 hours, to form a urethane intermediate, followed by addition of a base and reaction at about 20°C to 100°C for about 1 to 24 hours to form the oxazolidinone

5   composition. Alternatively, an epoxide can be reacted with an isocyanate in the presence of a catalyst, such as diethyl zinc, to form the oxazolidinone directly.

Suitable fluorochemical oxazolidinones and methods for their preparation are further described in U.S. Patent Nos. 5,025,052 and 5,099,026 (Crater et al.).

Other preferred fluorochemical repellents, useful both in topical treatments

10   and as polymer melt (or other bulk polymer) additives, include those described in U.S. Patent Nos. 3,899,563 (Oxenrider et al.), 4,219,625 (Mares et al.), 5,560,992 (Sargent et al.), and 5,681,963 (Liss); International Patent Publication Nos. WO 97/22576, WO 97/22659, and WO 97/22660 (E. I. du Pont de Nemours and Company); Japanese Patent Publication Nos. 3-041160 (Kao Corporation) and 9-

15   323956 (Wako Junyaku Kogyo Co.); and International Patent Publication No. WO 99/05345 (Minnesota Mining and Manufacturing Company).

Of these, particularly preferred are the fluorochemical group-containing derivatives of long-chain (preferably, having at least about 30 carbon atoms; more preferably, dimer and trimer, as defined below) acids, alcohols, and amines. A

20   preferred class of such derivatives includes the compounds or mixtures of compounds represented by the formulas:

$$\{(R_f)_n - Q - O - C(O)\}_p - A$$
$$\{(R_f)_n - Q - C(O) - O\}_p - A'$$
$$\{(R_f)_n - Q - N(R) - C(O)\}_p - A$$
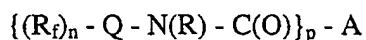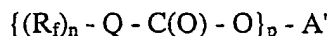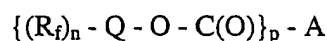
25      $$\{(R_f)_n - Q - C(O) - N(R)\}_p - A'$$

wherein R_f is a fluorinated alkyl group (which can optionally contain one or more catenary (in-chain) heteroatoms such as oxygen) bonded through carbon; n is 1 or 2; Q is a divalent or trivalent linking group or a covalent bond; p is 2 or more, up to the valency of A or A'; R is a hydrogen atom or is a substituted or unsubstituted

30   alkyl group; A is the residue of a dimer or trimer acid; and A' is the residue of a dimer diol, a dimer diamine, a trimer triol, or a trimer triamine. Preferably, R_f is a perfluoroalkyl group having from about 3 to about 20 carbon atoms (preferably,

-22-

from about 4 to about 12 carbon atoms); R is an alkyl group having from 1 to 6 carbon atoms; Q is $-SO_2N(R')(CH_2)_k-$, $-(CH_2)_k-$, $-CON(R')(CH_2)_k-$, or $-(CH_2)_kSO_2N(R')(CH_2)_k-$, where R' is hydrogen, phenyl, or a short chain (up to about 6 carbon atoms) alkyl group (preferably, methyl or ethyl), and each k is

5   independently an integer from 1 to about 20; A is the residue of a dimer acid; and A' is the residue of a dimer diol or dimer diamine. The esters and "reverse" esters are preferred over the amides and "reverse" amides.

        Such fluorochemical group-containing dimer and trimer acid esters can be prepared by heating a fluorochemical alcohol with either a dimer acid or a trimer

10   acid in the presence of a standard acid catalyst, or by first making an acid chloride of the dimer/trimer acid and then reacting the acid chloride with a fluorochemical alcohol at a slightly elevated temperature (for example, 50-60°C) in the presence of an acid scavenger. Fluorochemical group-containing "reverse" esters can be prepared by reacting a fluorochemical carboxylic acid with a dimer diol, using the

15   same synthetic procedure as described for preparing esters. Fluorochemical group-containing amides can be prepared by reacting a fluorochemical amine with a dimer or trimer acid by heating the components together neat at an elevated temperature (at least about 220°C), or by first making an acid chloride of the dimer/trimer acid and then reacting the acid chloride with a fluorochemical amine

20   at a slightly elevated temperature. Fluorochemical group-containing "reverse" amides can be prepared by reacting a fluorochemical carboxylic acid with a dimer amine, using the same synthetic procedure as described for preparing esters.

        The terms "dimer acid" and "trimer acid" refer to oligomerized unsaturated fatty acid products of relatively high molecular weight. The products are mixtures

25   comprising various ratios of a variety of large or relatively high molecular weight substituted cyclohexenecarboxylic acids, predominately 36-carbon dibasic acids (dimer acid) and 54-carbon tribasic acids (trimer acid), with no single structure sufficient to characterize each. Component structures can be acyclic, cyclic (monocyclic or bicyclic), or aromatic.

30   Dimer and trimer acids (for use in preparing the above-described fluorochemical repellents) can be prepared by condensing unsaturated monofunctional carboxylic acids such as oleic, linoleic, soya, or tall oil acid

through their olefinically unsaturated groups, in the presence of catalysts such as acidic clays. Dimer/trimer acids are commercially available from a variety of vendors, including Henkel Corporation/Emery Group (as Empol™ 1008, 1061, 1040 and 1043) and Unichema North America (as Pripol™ 1004 and 1009). Dimer

5   diols and diamines can be made from the corresponding dimer acid by methods well known in the art. Dimer diols are commercially available from Henkel Corp./Emery Group as Empol™ 1070 and 1075 diols. Dimer amines are commercially available from Witco Corp., for example, as Kemamine™ DP-3695 amine.

10

Insulating Materials

       Insulating materials that are suitable for topical treatment include materials that have relatively low surface and bulk conductivity and that are prone to static charge buildup. Such materials include both synthetic and naturally-occurring

15   polymers (or the reactive precursors thereof, for example, mono- or multifunctional monomers or oligomers) that can be either organic or inorganic in nature, as well as ceramics, glasses, and ceramic/polymer composites or ceramers (or the reactive precursors thereof).

       Suitable synthetic polymers (which can be either thermoplastic or

20   thermoset) include commodity plastics such as, for example, poly(vinyl chloride), polyethylenes (high density, low density, very low density), polypropylene, and polystyrene; engineering plastics such as, for example, polyesters (including, for example, poly(ethylene terephthalate) and poly(butylene terephthalate)), polyamides (aliphatic, amorphous, aromatic), polycarbonates (for example,

25   aromatic polycarbonates such as those derived from bisphenol A), polyoxymethylenes, polyacrylates and polymethacrylates (for example, poly(methyl methacrylate)), some modified polystyrenes (for example, styrene-acrylonitrile (SAN) and acrylonitrile-butadiene-styrene (ABS) copolymers), high-impact polystyrenes (SB), fluoroplastics, and blends such as poly(phenylene oxide)-

30   polystyrene and polycarbonate-ABS; high-performance plastics such as, for example, liquid crystalline polymers (LCPs), polyetherketone (PEEK),

-24-

polysulfones, polyimides, and polyetherimides; thermosets such as, for example, alkyd resins, phenolic resins, amino resins (for example, melamine and urea resins), epoxy resins, unsaturated polyesters (including so-called vinyl esters), polyurethanes, allylics (for example, polymers derived from

5   allyldiglycolcarbonate), fluoroelastomers, and polyacrylates; and the like and blends thereof. Suitable naturally occurring polymers include proteinaceous materials such as silk, wool, and leather; and cellulosic materials.

Thermoplastic and thermoset polymers, including those described above, are preferred insulating materials, as such polymers can either be topically treated

10   with the antistat/repellent combination or can be combined with it (in bulk) to form a blend. Thermoplastic polymers are more preferred in view of their melt processability. Preferably, the thermoplastic polymers are melt processable at elevated temperatures, for example, above about 150°C (more preferably, above about 250°C; even more preferably, above about 280°C; most preferably, above

15   about 320°C). Preferred thermoset polymers include polyurethanes, epoxy resins, and unsaturated polyesters. Preferred thermoplastic polymers include, for example, polypropylene, polyethylene, copolymers of ethylene and one or more alpha-olefins (for example, poly(ethylene-butene) and poly(ethylene-octene)), polyesters, polyurethanes, polycarbonates, polyetherimides, polyimides, polyetherketones,

20   polysulfones, polystyrenes, ABS copolymers, polyamides, fluoroelastomers, and blends thereof. More preferred are polypropylene, polyethylene, polyesters, poly(ethylene-octene), polyurethanes, polycarbonates, and blends thereof, with polypropylene, polyethylene, poly(ethylene-octene), polyurethanes, and blends thereof being most preferred.

25

Preparation and Use of Composition

Preferably, the composition of the invention can be prepared by (a) combining at least one ionic salt antistat, at least one fluorochemical repellent, and at least one thermoplastic polymer (optionally, along with other additives) and then

30   melt processing the resulting combination; or (b) combining at least one ionic salt antistat, at least one fluorochemical repellent, and at least one thermosetting polymer or ceramer or the reactive precursors thereof (optionally, along with other

additives) and then allowing the resulting combination to cure, optionally with the application of heat or actinic radiation. Alternative processes for preparing the composition include, for example, (c) applying a treatment composition comprising at least one ionic salt antistat and at least one fluorochemical repellent to at least a

5   portion of at least one surface of at least one insulating material; (d) dissolving at least one ionic salt antistat, at least one fluorochemical repellent, and at least one insulating material in at least one solvent and then casting or coating the resulting solution and allowing evaporation of the solvent, optionally with the application of heat; and (e) combining at least one ionic salt antistat, at least one fluorochemical

10   repellent, and at least one monomer (optionally, along with other additives) and then allowing polymerization of the monomer to occur, optionally in the presence of at least one solvent and optionally with the application of heat or actinic radiation. If desired, the antistat and repellent can be utilized separately, for example, one can be added prior to melt processing, and the other can then be

15   topically applied to the resulting melt-processed combination. Separate topical treatments, etc., are also possible.

        To form a melt blend by melt processing, the ionic salt antistat(s) and fluorochemical repellent(s) can be, for example, intimately mixed with pelletized or powdered polymer and then melt processed by known methods such as, for

20   example, molding, melt blowing, melt spinning, or melt extrusion. The antistat and repellent additives can be mixed directly with the polymer or they can be mixed with the polymer in the form of a "master batch" (concentrate) of the additives in the polymer. If desired, an organic solution of the additives can be mixed with powdered or pelletized polymer, followed by drying (to remove

25   solvent) and then by melt processing. Alternatively, the additives can be injected into a molten polymer stream to form a blend immediately prior to, for example, extrusion into fibers or films or molding into articles.

        After melt processing, an annealing step can be carried out to enhance the development of antistatic and repellent characteristics. In addition to, or in lieu of,

30   such an annealing step, the melt processed combination (for example, in the form of a film or a fiber) can also be embossed between two heated rolls, one or both of which can be patterned. An annealing step typically is conducted below the melt

temperature of the polymer (for example, in the case of polyamide, at about 150-
220°C for a period of about 30 seconds to about 5 minutes). In some cases, the
presence of moisture can improve the effectiveness of the ionic salt antistat(s),
although the presence of moisture is not necessary in order for antistatic

5   characteristics to be obtained.

The ionic salt antistat(s) and fluorochemical repellent(s) can be added to
thermoplastic or thermosetting polymer (or, alternatively, to other insulating
material) in amounts sufficient to achieve the desired antistatic and repellency
properties for a particular application. The amounts can be determined empirically

10   and can be adjusted as necessary or desired to achieve the antistatic and repellency
properties without compromising the properties of the polymer (or other insulating
material). Generally, the ionic salt antistat(s) and the fluorochemical repellent(s)
can each be added in amounts ranging from about 0.1 to about 10 percent by
weight (preferably, from about 0.5 to about 2 percent; more preferably, from about

15   0.75 to about 1.5 percent) based on the weight of polymer (or other insulating
material).

In topical treatment of an insulating material, the combination of ionic salt
antistat(s) and fluorochemical repellent(s) can be employed alone or in the form of
aqueous suspensions, emulsions, or solutions, or as organic solvent (or organic

20   solvent/water) solutions, suspensions, or emulsions. Useful organic solvents
include chlorinated hydrocarbons, alcohols (for example, isopropyl alcohol), esters,
ketones (for example, methyl isobutyl ketone), and mixtures thereof. Generally,
the solvent solutions can contain from about 0.1 to about 50 percent, or even up to
about 90 percent, by weight non-volatile solids (based on the total weight of the

25   components). Aqueous suspensions, emulsions, or solutions are generally
preferred and generally can contain a non-volatile solids content of about 0.1 to
about 50 percent, preferably, about 1 to about 10 percent, by weight (based on the
total weight of the components). Alternatively, however, topical treatment can be
carried out by applying (to at least a portion of at least one surface of at least one

30   insulating material) a topical treatment composition that comprises at least one
ionic salt antistat that is liquid at the use or treatment temperature. Such a topical
treatment process can involve the use of the neat liquid ionic salt antistat, without

added solvent, and is thus preferred from an environmental perspective over the use of organic solvent solutions of the antistat/repellent combination.

The topical treatment compositions comprising the antistat/repellent combination can be applied to an insulating material by standard methods such as,

5   for example, spraying, padding, dipping, roll coating, brushing, or exhaustion (optionally followed by the drying of the treated material to remove any remaining water or solvent). The material can be in the form of molded or blown articles, sheets, fibers (as such or in aggregated form, for example, yarn, toe, web, or roving, or in the form of fabricated textiles such as carpets), woven and nonwoven

10   fabrics, films, etc. If desired, the antistat/repellent combination can be co-applied with conventional fiber treating agents, for example, spin finishes or fiber lubricants.

The topical treatment compositions can be applied in an amount sufficient to achieve the desired antistatic and repellency properties for a particular

15   application. This amount can be determined empirically and can be adjusted as necessary or desired to achieve the antistatic and repellency properties without compromising the properties of the insulating material.

Any of a wide variety of constructions can be made from the composition of the invention, and such constructions will find utility in any application where

20   some level of antistatic and repellency characteristics is required. For example, the composition of the invention can be used to prepare films and molded or blown articles, as well as fibers (for example, melt-blown or melt-spun fibers, including microfibers) that can be used to make woven and nonwoven fabrics. Such films, molded or blown articles, fibers, and fabrics exhibit antistatic and water and oil

25   repellency (and soil resistance) characteristics under a variety of environmental conditions and can be used in a variety of applications.

For example, molded articles comprising the composition of the invention can be prepared by standard methods (for example, by high temperature injection molding) and are particularly useful as, for example, headlamp covers for

30   automobiles, lenses (including eyeglass lenses), casings or circuit boards for electronic devices (for example, computers), screens for display devices, windows (for example, aircraft windows), and the like. Films comprising the composition of

the invention can be made by any of the film making methods commonly employed in the art. Such films can be nonporous or porous (the latter including films that are mechanically perforated), with the presence and degree of porosity being selected according to the desired performance characteristics. The films can be

5   used as, for example, photographic films, transparency films for use with overhead projectors, tape backings, substrates for coating, and the like.

Fibers comprising the composition of the invention can be used to make woven or nonwoven fabrics that can be used, for example, in making medical fabrics, medical and industrial apparel, fabrics for use in making clothing, home

10   furnishings such as rugs or carpets, and filter media such as chemical process filters or respirators. Nonwoven webs or fabrics can be prepared by processes used in the manufacture of either melt-blown or spunbonded webs. For example, a process similar to that described by Wente in "Superfine Thermoplastic Fibers," Indus. Eng'g Chem. 48, 1342 (1956) or by Wente et al. in "Manufacture of Superfine

15   Organic Fibers," Naval Research Laboratories Report No. 4364 (1954) can be used. Multi-layer constructions made from nonwoven fabrics enjoy wide industrial and commercial utility, for example, as medical fabrics. The makeup of the constituent layers of such multi-layer constructions can be varied according to the desired end-use characteristics, and the constructions can comprise two or more

20   layers of melt-blown and spunbonded webs in many useful combinations such as those described in U.S. Patent Nos. 5,145,727 (Potts et al.) and 5,149,576 (Potts et al.). In multi-layer constructions, the ionic salt antistat(s) and fluorochemical repellent(s) can be used in combination in one or more layers, or each can be independently segregated in one or more layers. For example, in a

25   spunbonded/melt-blown/spunbonded ("SMS") three-layer construction, the ionic salt antistat(s) can be used in one or both spunbonded layers, and the fluorochemical repellent(s) can be used in the melt-blown layer, to impart both antistatic and repellency characteristics to the overall construction.

The ionic salt antistat(s) and fluorochemical repellent(s) used in the

30   composition of the invention can also find utility as additives to coatings (for example, polymer or ceramer coatings). Such coatings can be antistatic, water- and oil-repellent, and scratch-resistant (as well as soil-resistant) and can be used in the

-29-

photographic industry or as protective coatings for optical or magnetic recording media.

If desired, the composition of the invention can further contain one or more conventional additives commonly used in the art, for example, dyes, pigments,

5   antioxidants, ultraviolet stabilizers, flame retardants, surfactants, plasticizers, tackifiers, fillers, and mixtures thereof. In particular, performance enhancers (for example, polymers such as polybutylene) can be utilized to improve the antistatic and/or repellency characteristics in, for example, melt additive polyolefin applications.

10   Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention. In the examples, where weight percent or parts by weight are indicated, these are based on the weight of the entire composition unless

15   indicated otherwise.

EXAMPLES

GLOSSARY

20

Antistats

HTS 905 and 905A - Larostat™ HTS 905 or 905A (anhydrous), $C_8H_{17}N^+(CH_3)_2CH_2CH_2OH$ $^-OSO_2CH_3$, available from BASF, Gurnee, Illinois.

HTS-904 – 3-(2-hydroxyethyl)-1-methyl-2-undecylimidazolinium p-

25   toluenesulfonate, available from BASF, Gurnee, Illinois.

Lithium perfluorobutanesulfonate – available from 3M, St. Paul, MN.

Anstex™ SA-300 – an antistatic melt additive

agent, octadecanoic acid 2-[(2-hydroxyethyl)octadecylamino]ethyl ester, available from TOHO chemical Industry Co., Japan.

30   Aluminum Stearate – available from All Chemie Ltd., Mt. Pleasant, SC.

Lithium Stearate – available from ACROS Organics USA, Pittsburg, PA.

Glycerol Monostearate – available from Sigma-Aldrich, Milwaukee, WI.

Aliquat™ 336 – Methyltrioctylammonium chloride, available from Sigma-Aldrich, Milwaukee, WI, or from Henkel Corp., Ambler, PA.

Starting Materials for Antistats

5   **HQ-115** – LiN(SO$_2$CF$_3$)$_2$ available from 3M, St. Paul, MN.

PBSF – Perfluorobutanesulfonyl fluoride, available from Sigma-Aldrich, Milwaukee, Wi.

Lithium triflate – Lithium trifluoromethanesulfonate, available from Sigma-Aldrich, Milwaukee, Wi.

10   **FC-24** – Trifluoromethanesulfonic acid, available from 3M, St. Paul, MN.

FC-754 – Trimethyl-3-perfluorooctylsulfonamidopropylammonium chloride, available from 3M, St. Paul, MN.

FC-94 – Lithium perfluorooctanesulfonate, available from 3M, St. Paul, MN.

15   **Cetylpyridinium chloride monohydrate** – 1-Hexadecylpyridinium chloride, available from Research Organics, Cleveland, OH.

1,3-Ethylmethylimidazolium chloride – Available from Sigma-Aldrich, Milwaukee, WI.

Silver triflate – Silver trifluoromethanesulfonate, available from Sigma-Aldrich, Milwaukee, WI.

20   **AgBF$_4$** – Silver tetrafluoroborate, available from Sigma-Aldrich, Milwaukee, WI.

NH$_4$PF$_6$ – Ammonium hexafluorophosphate, available from Sigma-Aldrich, Milwaukee, WI.

25   **Acetylcholine chloride** – CH$_3$CO$_2$CH$_2$CH$_2$N(CH$_3$)$_3$Cl, available from Research Organics, Cleveland, OH.

Choline chloride – HOCH$_2$CH$_2$N(CH$_3$)$_3$Cl, available from Sigma-Aldrich, Milwaukee, WI.

30   **Fluorochemical Repellents**

FC-808 – A fluorochemical emulsion of a polymeric fluoroaliphatic ester (80 weight percent in water) for fluid repellency, available from 3M, St. Paul, MN.

Starting Materials for Fluorochemical Repellents

MeFOSE alcohol - $C_8F_{17}SO_2N(CH_3)CH_2CH_2OH$,

having an equivalent weight of 540, made in two stages by reacting POSF

perfluorooctanesulfonyl fluoride with methylamine and ethylenechlorohydrin,

using a procedure similar to that described in Example 1 of U.S. Pat. No. 2,803,656

(Ahlbrecht et al.).

Empol™ 1008 acid - a distilled and hydrogenated dimer acid based on oleic

acid, having an acid equivalent weight of 305 as determined by titration,

commercially available from Henkel Corp./Emery Group, Cincinnati, Ohio.

Pripol™ 1048 acid - a hydrogenated distilled

dimer/trimer acid based on oleic acid, commercially available from Unichema

North America, Chicago, Illinois.

Thermoplastic Polymers

PP3505 - ESCORENE™ PP3505 polypropylene, having a 400 melt index

flow rate, available from Exxon Chemical Co., Baytown, Texas.

Montell H422PP – a granular polypropylene polymer (with peroxide)

having an 850 melt flow index, available from Montell North America,

Wilmington, DE.

PB0200 – polybutylene, available from Shell Chemical Co., Houston,

Texas.

PB8340 – copolymer of 1-butene and ethylene, available from Shell

Chemical Co., Houston, Texas.

PE6806 - ASPUN™ 6806 polyethylene, having a melt flow index of 105

g/10 min (as measured by Test Method ASTM D-1238) and having a peak melting

point of 124.8°C, available from Dow Chemical Co., Midland, Michigan.

PS440-200 - MORTHANE™ PS440-200 urethane, available from Morton

Thiokol Corp., Chicago, Illinois.

TEST METHODS

Test Method I – Melting Point Determination

　　　　　The melting points of salts were determined by differential scanning
5　calorimetry (DSC) using a 20°C per minute temperature ramp. The peak
maximum of the melt transition was taken as the melting point (Tm). Where
multiple melt transitions were observed, the peak associated with the largest area
melt transition was taken as the melting point.

Test Method II – Onset of Thermal Decomposition Determination

10　　　The onset of thermal decomposition of each salt was determined by thermal
gravimetric analysis (TGA) under an inert nitrogen atmosphere using a 10°C per
minute temperature ramp. The value of the onset temperature was determined by
finding the intersection of the extrapolated tangent at the baseline preceding onset
15　and the extrapolated tangent at the inflection point associated with the step change
in sample weight.

Test Method III – Static Charge Dissipation Test

　　　　　The static charge dissipation characteristics of nonwoven fabrics, films, and
20　molded sheets were determined with this method. The test materials were cut into
9 cm by 12 cm samples and conditioned at relative humidities (RH) of about 10
percent, 25 percent, and 50 percent for at least 12 hours. The materials were tested
at temperatures that ranged from 22-25°C. The static charge dissipation time was
measured according to Federal Test Method Standard 10113, Method 4046,
25　"Antistatic Properties of Materials", using an ETS Model 406C Static Decay Test
Unit (manufactured by Electro-Tech Systems, Inc., Glenside, PA). This apparatus
induces an initial static charge (Average Induced Electrostatic Charge) on the
surface of the flat test material by using high voltage (5000 volts), and a fieldmeter
allows observation of the decay time of the surface voltage from 5000 volts (or
30　whatever the induced electrostatic charge was) to 10 percent of the initial induced
charge. This is the static charge dissipation time. The lower the static charge
dissipation time, the better the antistatic properties are of the test material. All

reported values of the static charge dissipation times in this invention are averages (Average Static Decay Rate) over at least 3 separate determinations. Values reported as > 10, > 60, or > 100 seconds indicate that the material tested has an initial static charge which cannot be removed by surface conduction and is not

5   antistatic. When the material tested did not accept a charge of about 3000 volts or more, it was not considered to have charged sufficiently to be antistatic.

Test Method IV – Surface Resistivity Test

This test was conducted according to the procedure of ASTM Standard D-

10   257, "D.C. Resistance or Conductance of Insulating Materials". The surface resistivity was measured under the conditions of this test method using an ETS Model 872 Wide Range Resistance Meter fitted with a Model 803B probe (Electro-Tech Systems, Inc., Glenside, PA). This apparatus applies an external voltage of 100 volts across two concentric ring electrodes contacting the flat test material, and

15   provides surface resistivity readings in ohm/square units.

Test Method V - Water Repellency Test

Nonwoven web samples were evaluated for water repellency using 3M Water Repellency Test V for Floorcoverings (February 1994), available from 3M

20   Company. In this test, samples are challenged to penetrations by blends of deionized water and isopropyl alcohol (IPA). Each blend is assigned a rating number as shown below:

Water Repellency Rating Number	Water/IPA Blend (% by volume)
0	100% water
1	90/10 water/IPA
2	80/20 water/IPA
3	70/30 water/IPA
4	60/40 water/IPA
5	50/50 water/IPA
6	40/60 water/IPA
7	30/70 water/IPA

25

30

8	20/80 water/IPA
9	10/90 water/IPA
10	100% IPA

In running the Water Repellency Test, a nonwoven web or film sample is placed on a flat, horizontal surface. Five small drops of water or a water/IPA mixture are gently placed at points at least two inches apart on the sample. If, after observing for ten seconds at a 45° angle, four of the five drops are visible as a sphere or a hemisphere, the nonwoven web or film sample is deemed to pass the test. The reported water repellency rating corresponds to the highest numbered water or water/IPA mixture for which the nonwoven sample passes the described test.

It is desirable to have a water repellency rating of at least 4, preferably at least 6.

Test Method VI - Oil Repellency Test

Nonwoven web or film samples were evaluated for oil repellency using 3M Oil Repellency Test III (February 1994), available from 3M Company, St. Paul, Minnesota. In this test, samples are challenged to penetration or droplet spread by oil or oil mixtures of varying surface tensions. Oils and oil mixtures are given a rating corresponding to the following:

Oil Repellency Rating Number	Oil Composition
0	(fails Kaydol™ mineral oil)
1	Kaydol™ mineral oil
2	65/35 (vol) mineral oil/n-hexadecane
3	n-hexadecane
4	n-tetradecane
5	n-dodecane
6	n-decane

| 7 | n-octane |
| 8 | n-heptane |

The Oil Repellency Test is run in the same manner as is the Water

Repellency Test, with the reported oil repellency rating corresponding to the

highest oil or oil mixture for which the nonwoven web or film sample passes the

test.

It is desirable to have an oil repellency rating of at least 1, preferably at

least 3.

PREPARATION AND CHARACTERIZATION OF ANTISTATS FOR MELTING POINT AND THERMAL DECOMPOSITION

Antistat 1

Synthesis of Triethylammonium bis(perfluoroethanesulfonyl)imide,

$Et_3N^+H \ ^-N(SO_2C_2F_5)_2$

This compound was prepared essentially according to the method described

in US 5,874,616 (Howells, et al), Example 3, except that the procedure was

terminated once the methylene chloride solvent was evaporated. The resulting

product was characterized for melting point (T_m) according to Test Method I and

for onset of thermal decomposition (T_d) according to Test Method II. Results are

shown in Table 1.

Antistat 2

Synthesis of Tetraethylammonium trifluoromethanesulfonate, $CF_3SO_3^- \ ^+NEt_4$

In a 2L flask, 300 g of CF_3SO_3H (FC-24) was charged. The acid was

neutralized by slow addition of about 800g Et_4NOH aqueous solution (35%) until

the pH reached about 6. A white solid (560g) was obtained after drying by rotary

evaporation, then under high vacuum. The solid was re-crystallized from

chloroform-heptane to give 520g pure product. This product was also characterized

for melting point (T_m) according to Test Method I and for onset of thermal

decomposition (T_d) according to Test Method II. Results are shown in Table 1.

Antistat 3

Synthesis of Tetraethylammonium bis(trifluoromethanesulfonyl)imide, $(CF_3SO_2)_2N^-$ $^+NEt_4$ in Water-CH_2Cl_2 Mixed Solvent

In a 1L flask, 50 g of $(CF_3SO_2)_2N^-$ Li^+ (HQ-115) was dissolved in 50 g of
deionized water. The solution was combined with 89 g of 35% Et_4NOH aqueous
solution under N_2. Solid precipitated during the addition, which was dissolved by
the addition of 50 g CH_2Cl_2. The bottom organic layer was isolated. The aqueous
solution was extracted with another 50 g of CH_2Cl_2. The combined organic
solution was washed with water (2 x 25 mL), and volatiles were removed by rotary
evaporation. Re-crystallization of the crude product from CH_3OH-H_2O gave 70g of
white solid after full vacuum drying. The product was characterized for melting
point (T_m) according to Test Method I and for onset of thermal decomposition (T_d)
according to Test Method II. Results are shown in Table 1.

Antistat 4

Synthesis of Tetrabutylammonium bis(trifluoromethanesulfonyl)imide, $(C_4H_9)_4N^+$ $^-N(SO_2CF_3)_2$

This compound was prepared by reacting $(C_4H_9)_4N^+Br^-$ (Sigma-Aldrich,
Milwaukee, WI) with approximately a 10% molar excess of Li^+ $^-N(SO_2CF_3)_2$ (HQ-
115) essentially according to the procedure described in Example 18 of U.S. Patent
No. 5,554,664 (Lamanna et al). The resulting product was characterized for melting
point (T_m) according to Test Method I and for onset of thermal decomposition (T_d)
according to Test Method II. Results are shown in Table 1.

Table 1. Melting Point (T_m) and Onset of Thermal Decomposition (T_d) Values

Antistat	Formula	T_m (°C)	T_d (°C)
1	Et_3N^+H $^-N(SO_2C_2F_5)_2$	-10	351
2	$CF_3SO_3^-$ $^+NEt_4$	133	371
3	$(CF_3SO_2)_2N^-$ $^+NEt_4$	8	426
4	$(C_4H_9)_4N^+$ $^-N(SO_2CF_3)_2$	93	401
23	$(C_8H_{17})_3N^+(CH_3)$ Cl^-	< 28	177

The data in Table 1 shows that Antistats 1-4, which comprise weakly coordinating fluoroorganic anions, exhibited much greater thermal stability than Antistat 23, which has the more strongly coordinating chloride anion.

Antistat 5

Synthesis of 1-Hexadecylpyridinium Bis(perfluoroethanesulfonyl)imide, n-$C_{16}H_{33}$-cyc-$N^+C_5H_5$ $^-N(SO_2C_2F_5)_2$

This compound was prepared essentially according to the method of Antistat 6, except that 85.1g of Li^+ $^-N(SO_2C_2F_5)_2$ (HQ-115) was employed as the anion precursor instead of Li^+ $^-OSO_2C_4F_9$. The product was characterized for melting point (T_m) according to Test Method I and for onset of thermal decomposition (T_d) according to Test Method II. Results are shown in Table 2.

Antistat 6

Synthesis of 1-Hexadecylpyridinium Perfluorobutanesulfonate, n-$C_{16}H_{33}$-cyc-$N^+C_5H_5$ $^-OSO_2C_4F_9$

Cetylpyridinium chloride monohydrate (75g) was dissolved in 800ml water with gentle heating and magnetic stirring. To this solution was added 67.3g of Li^+ $^-OSO_2C_4F_9$ (prepared by hydrolysis of $C_4F_9SO_2F$ [PBSF] with LiOH) dissolved in 600mL of water with stirring. The resulting product precipitated immediately and was isolated by suction filtration. The product was washed with copious amounts of water and then dried initially by suction and then in vacuo at 10^{-2} Torr, 40°C.

The product was characterized for melting point (T_m) according to Test Method I and for onset of thermal decomposition (T_d) according to Test Method II. Results are shown in Table 2.

5   **Antistat 7**

Synthesis of 1-Hexadecylpyridinium Perfluorooctanesulfonate,

n-$C_{16}H_{33}$-*cyc*-$N^+C_5H_5$ $^-OSO_2C_8F_{17}$
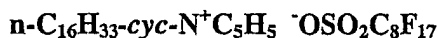
This compound was prepared essentially according to the method of Antistat 6, except that 111.3g of Li^+ $^-OSO_2C_8F_{17}$ (FC-94) was employed as the

10   anion precursor. The resulting product was characterized for melting point (T_m) according to Test Method I and for onset of thermal decomposition (T_d) according to Test Method II. Results are shown in Table 2.

Antistat 8

15   **Synthesis of n-Butylpyridinium Bis(trifluoromethanesulfonyl)imide,**

n-C_4H_9-*cyc*-$N^+C_5H_5$ $^-N(SO_2CF_3)_2$

A solution of 50g Li^+ $^-N(SO_2CF_3)_2$ (HQ-115) (287 g/mol, 0.174 mol) and 100 ml DI water was prepared. Another solution of 30g butylpyridinium chloride (171.6 g/mol, 0.174) and 100 ml deionized water was prepared. The two solutions

20   were added to a separatory funnel along with 200 ml methylene chloride. The mixture was thoroughly shaken, and the phases were allowed to separate. The organic phase was isolated and washed with 3 x 200 ml deionized water. The organic layer was then concentrated by reduced pressure distillation on a rotary evaporator. The resulting yellow oil was vacuum dried at 120C overnight to afford

25   70g product (97% yield). The product was characterized for melting point (T_m) according to Test Method I and for onset of thermal decomposition (T_d) according to Test Method II. Results are shown in Table 2.

Antistat 9

Synthesis of n-Butylpyridinium Perfluorobutanesulfonate,

$n\text{-}C_4H_9\text{-}cyc\text{-}N^+C_5H_5 \ ^-OSO_2C_4F_9$

A solution of 20g butylpyridinium chloride (171.6 g/mol, 0.116 mol) was
5   made with 100 ml deionized water. A similar solution was prepared using 35.7g

$Li^+ \ ^-OSO_2C_4F_9$ (prepared by hydrolysis of $C_4F_9SO_2F$ [PBSF] with LiOH) (306

g/mol, 0.116 mol) and 100 ml water. The two solutions were added to a separatory

funnel along with 200 ml methylene chloride. The mixture was thoroughly shaken,

and the phases were allowed to separate. The organic phase was isolated and

10   washed with 200 ml DI water. The mixture was slow to separate, consequently

further washings were not done. The organic layer was concentrated by reduced

pressure distillation on a rotary evaporator, and then dried under vacuum at 130°C

overnight. The resulting yellow oil weighed 44g (87% yield) and was

characterized for melting point (T_m) according to Test Method I and for onset of

15   thermal decomposition (T_d) according to Test Method II. Results are shown in

Table 2.

Table 2. Melting Point (T_m) and Onset of Thermal Decomposition (T_d) Values

Antistat	Formula	T_m (°C)	T_d (°C)
5	$n\text{-}C_{16}H_{33}\text{-}cyc\text{-}N^+C_5H_5 \ ^-N(SO_2C_2F_5)_2$	34	396
6	$n\text{-}C_{16}H_{33}\text{-}cyc\text{-}N^+C_5H_5 \ ^-OSO_2C_4F_9$	95	357
7	$n\text{-}C_{16}H_{33}\text{-}cyc\text{-}N^+C_5H_5 \ ^-OSO_2C_8F_{17}$	93	364
8	$n\text{-}C_4H_9\text{-}cyc\text{-}N^+C_5H_5 \ ^-N(SO_2CF_3)_2$	33	430
9	$n\text{-}C_4H_9\text{-}cyc\text{-}N^+C_5H_5 \ ^-OSO_2C_4F_9$	63	391

20   Table 2 shows that the pyridinium cation-containing Antistats 5-9, which

comprise weakly coordinating fluoroorganic anions, exhibited very good thermal

stability.

Antistat 10

Synthesis of 1,3-Ethylmethylimidazolium Bis(trifluoromethanesulfonyl)imide, CH_3-cyc-$(N^+C_2H_2NCH)CH_2CH_3$ $^-N(SO_2CF_3)_2$

1,3-Ethylmethylimidazolium chloride (50.0g) and $LiN(SO_2CF_3)_2$ (HQ-115)

5 (102.8g) were combined in 500mL of water with magnetic stirring. An immiscible light yellow oil of low viscosity separated as a lower liquid phase. The mixture was transferred to a separatory funnel, and 500mL of methylene chloride was added. The mixture was shaken vigorously and allowed to phase separate. The lower organic phase was isolated and washed with two additional 500mL portions of

10 water. The washed methylene chloride phase was isolated, dried over anhydrous aluminum oxide beads, filtered by suction and vacuum stripped at 30-100°C , 20 - 10^{-3} Torr to remove all volatiles. A total of 112.2g (84% yield) of light yellow oil of high purity was obtained, which was identified as the title compound by ^1H and ^{19}F NMR. The product was also characterized for melting point (T_m) according to

15 Test Method I and for onset of thermal decomposition (T_d) according to Test Method II. Results are shown in Table 3.

Antistat 11

Synthesis of 1,3-Ethylmethylimidazolium Nonafluorobutanesulfonate,

20 CH_3-cyc-$(N^+C_2H_2NCH)CH_2CH_3$ $^-OSO_2C_4F_9$

1,3-Ethylmethylimidazolium chloride (49.1g) and $LiOSO_2C_4F_9$ (107.6g, prepared by hydrolysis of $C_4F_9SO_2F$ with LiOH) were combined in 500mL of water with magnetic stirring. A homogeneous aqueous solution was formed, which was transferred to a separatory funnel, combined with 500mL of CH_2Cl_2 and

25 worked up essentially according to the procedure for Antistat 10. After vacuum stripping all volatiles, a total of 65.0g (47% yield) of light yellow oil of high purity was obtained, which was identified as the title compound by ^1H and ^{19}F NMR. The product was also characterized for melting point (T_m) according to Test Method I and for onset of thermal decomposition (T_d) according to Test Method II. Results

30 are shown in Table 3.

Antistat 12

**Synthesis of 1,3-Ethylmethylimidazolium trifluoromethanesulfonate,
CH$_3$-*cyc*-(N$^+$C$_2$H$_2$NCH)CH$_2$CH$_3$ $^-$OSO$_2$CF$_3$**

1,3-Ethylmethylimidazolium chloride (29g, 0.199 mole) was dissolved in

5   100 ml of water and added to solution of 50g silver triflate (0.195 mol) in 200g

water with stirring. The resulting silver chloride precipitate was removed by

filtration, and the solids were washed with 100ml of deionized water. The filtrate

was concentrated on a rotary evaporator and further dried at 75^{0}C overnight to

provide 47.5g of a light green oil that was characterized by ^{1}H and ^{19}F NMR. The

10   product was also characterized for melting point (T$_m$) according to Test Method I

and for onset of thermal decomposition (T$_d$) according to Test Method II. Results

are shown in Table 3.

Antistat 13

15   **Synthesis of 1,3-Ethylmethylimidazolium Tetrafluoroborate,
CH$_3$-*cyc*-(N$^+$C$_2$H$_2$NCH)CH$_2$CH$_3$ BF$_4$$^-$**

Separate solutions of 49.6 g AgBF4 (194.68g/mol, 0.255 mol) in 200 ml

distilled water, and 37.35g 1,3-ethylmethylimidazolium chloride (146.62 g/mol,

0.255 mol) in 200 ml distilled water were prepared. The two solutions were mixed

20   together, instantly forming a white precipitate. The precipitate was allowed to

settle, followed by filtration through a D-frit. The filtrate was concentrated, but not

to dryness, and allowed to stand at room temperature overnight. The next morning

a black precipitate was observed to have fallen out of solution. The solution was

passed through filter paper to removed the small amount of solid. The remaining

25   water was removed by reduced pressure distillation on a rotary evaporator. The

remaining oil was dissolved in 200 ml acetonitrile. More insoluble black

precipitate was formed and was filtered out of the solution. The resulting yellow

filtrate was concentrated on the rotary evaporator, and the resulting oil was dried

overnight under vacuum at 75C. The isolated weight of product was 40g (79%

30   yield). The product was characterized for melting point (T$_m$) according to Test

Method I and for onset of thermal decomposition (T$_d$) according to Test Method II.

Results are shown in Table 3.

Antistat 14

Synthesis of 1,3-Ethylmethylimidazolium Hexafluorophosphate,

CH_3-cyc-($N^+C_2H_2NCH)CH_2CH_3$ PF_6^-

5   A solution of 500 ml acetonitrile and 73.1g 1,3-ethylmethylimidazolium chloride (146.6 g/mol, 0.498 mol) was prepared in a 1L flask. Another solution of 250 ml acetonitrile and 81.1g NH_4PF_6 (163 g/mol, 0.498 mol) was similarly prepared and added to the former solution. A white precipitate instantly formed on mixing of the two solutions. The flask was chilled to near 0°C for 1 hour followed

10   by filtration through high purity Celite™ filter agent using a D-frit. The solvent was removed from the filtrate by reduced pressure distillation on a rotary evaporator. The resulting ionic salt was dried under vacuum at 75C overnight. The isolated weight of the ionic salt product was 114g (89% yield). The product was characterized for melting point (T_m) according to Test Method I and for onset

15   of thermal decomposition (T_d) according to Test Method II. Results are shown in Table 3.

Table 3. Melting point (T_m) and Onset of Thermal Decomposition (T_d) Values

Antistat	Formula	T_m (°C)	T_d (°C)
10	CH_3-cyc-($N^+C_2H_2NCH)CH_2CH_3$ $^-N(SO_2CF_3)_2$	-18	450
11	CH_3-cyc-($N^+C_2H_2NCH)CH_2CH_3$ $^-OSO_2C_4F_9$	18	410
12	CH_3-cyc-($N^+C_2H_2NCH)CH_2CH_3$ $^-OSO_2CF_3$	-16	429
13	CH_3-cyc-($N^+C_2H_2NCH)CH_2CH_3$ BF_4^-	7	420
14	CH_3-cyc-($N^+C_2H_2NCH)CH_2CH_3$ PF_6^-	70	490

20   The data of Table 3 show that the imidazolium cation-containing antistats, which comprise weakly coordinating fluoroorganic anions, all exhibited excellent thermal stability, with all T_d values greater than 400°C.

Antistat 15

Synthesis of 1-Dodecyl-2-ethyl-3-[2-hydroxyethyl]imidazolinium Toluenesulfonate,

$C_{12}H_{25}$-cyc-[$N^+C_2H_4N(CH_2CH_2OH)C]C_2H_5$ $^-OSO_2C_6H_4CH_3$

5   A 142.2 g sample of 2-ethyl-3-[2-hydroxyethyl]imidazoline (prepared essentially as described in U.S. Pat. No. 4,014,880) was combined with 340 g of 1-dodecyl toluenesulfonate (prepared essentially as described in Organic Synthesis, Collected Volume 3, p. 336 (1955) in a 1 liter three-neck round bottom flask and heated at a temperature of 75°C with stirring for 4 hours. The resulting

10   imidazolinium salt was transferred to a container for storage.

Antistat 16

Synthesis of Octyldimethyl-2-hydroxyethylammonium bis(trifluoromethylsulfonyl)imide, $C_8H_{17}N^+(CH_3)_2CH_2CH_2OH$ $^-N(SO_2CF_3)_2$

15   A 19.2g sample of $C_8H_{17}N^+(CH_3)_2CH_2CH_2OH$ $^-OSO_2CH_3$ (HTS 905A) was combined with 15.7g $LiN(SO_2CF_3)_2$ (HQ-115) in 120mL of water. After agitating the mixture, a clear, immiscible oil separated as a lower liquid phase. The mixture was transferred to a separatory funnel and 125mL of methylene chloride was added. The mixture was shaken vigorously and allowed to phase separate.

20   The lower organic phase was isolated and washed with two additional 125mL portions of water. The washed methylene chloride phase was isolated, dried over anhydrous aluminum oxide beads, filtered by suction and vacuum stripped at 30-100°C, 20 - 10^{-3} Torr to remove all volatiles. A colorless oil (22.6 g, 85% yield) of high purity was obtained, which was identified as the title compound by ^1H, ^{13}C

25   and ^{19}F NMR. The product was also characterized for melting point (T_m) according to Test Method I and for onset of thermal decomposition (T_d) according to Test Method II. Results are shown in Table 4.

Antistat 17

30   **Synthesis of Octyldimethyl-2-hydroxyethylammonium perfluorobutanesulfonate, $C_8H_{17}N^+(CH_3)_2CH_2CH_2OH$ $^-OSO_2C_4F_9$**

A 118.5g (0.399 mol) sample of $C_8H_{17}N^+(CH_3)_2CH_2CH_2OH\ ^-OSO_2CH_3$
(HTS 905A) was dissolved in about 250 ml of water and 123.9g (0.399 mol) of
$LiOSO_2C_4F_9$ (prepared by hydrolysis of $C_4F_9SO_2F$ [PBSF] with LiOH) was
dissolved in about 100 ml of water. The two solutions were added to a separatory
5   funnel and the mixture was shaken vigorously. Next 200 ml of methylene chloride
was added to the funnel and the contents were shaken and allowed to phase
separate. The lower methylene chloride layer was washed twice with about 200 ml
of water and concentrated on a rotary evaporator at about 85^0C for about 45
minutes to yield an off-white solid product, which was characterized by ^{1}H and
10   [13]C nuclear magnetic resonance spectroscopy (NMR). The product was also
characterized for melting point (T_m) according to Test Method I and for onset of
thermal decomposition (T_d) according to Test Method II. Results are shown in
Table 4.

15   **Antistat 18**

Synthesis of Octyldimethyl-2-hydroxyethylammonium

trifluoromethanesulfonate, $C_8H_{17}N^+(CH_3)_2CH_2CH_2OH\ ^-OSO_2CF_3$

Into 30g of acetonitrile in a 125 ml Erlenmeyer flask was dissolved with
heating 29.7g (0.1 mole) HTS-905A ($C_8H_{17}N^+(CH_3)_2CH_2CH_2OH\ ^-O_3SCH_3$) and
20   then cooled in an ice bath for 10 minutes. In another 125ml Erlenmeyer flask was
dissolved with heating 15.6g (0.1mole) lithium triflate into 30 ml of acetonitrile.
Next, the lithium triflate solution was added over a period of about 1 minute to the
stirred, cooled HTS-905A solution with generation of a white precipitate. About 2
ml of acetonitrile was used to rinse the Erlenmeyer flask that held the lithium
25   triflate solution, and this was also added to the HTS-905A solution. The resulting
reaction mixture was allowed to stir for about 10 minutes and was then vacuum
filtered through a pad of Celite™ filter agent on a 125ml Buchner funnel with a C
porosity frit. The reaction flask and Celite™ pad were washed with an additional
30 g of ice-cold acetonitrile. The filtrate was concentrated on a rotary evaporator at
30   about 50 mm Hg with a bath temperature of about 85^0C for about 45 minutes to
yield 24.5g of a clear solid product, which was characterized by ^{1}H and ^{13}C NMR.
The product was also characterized for melting point (T_m) according to Test

Method I and for onset of thermal decomposition (T_d) according to Test Method II. Results are shown in Table 4.

Antistat 19

5   **Synthesis of Octyldimethyl-2-hydroxyethylammonium tris(trifluoromethanesulfonyl)methide, $C_8H_{17}N^+(CH_3)_2CH_2CH_2OH \ ^- C(SO_2CF_3)_3$**

A 20.0g sample of $C_8H_{17}N^+(CH_3)_2CH_2CH_2OH \ ^-OSO_2CH_3$ (HTS 905) was combined with 29.6g $HC(SO_2CF_3)_3$ (prepared as described in Example 1 of U.S.

10   Patent No. 5,554,664 (Lamanna et al.) in 250 mL of water. After agitating the resulting mixture, a clear, viscous, pale yellow, immiscible oil separated as a lower liquid phase. The mixture was transferred to a separatory funnel, combined with 300mL of methylene chloride, and worked up essentially according to the procedure Antistat 16. After vacuum stripping all volatiles, a total of 29.0g (79%

15   yield) of pale yellow oil product was obtained, which was identified as the title compound by ^1H and ^{19}F NMR. Estimated purity from the NMR analysis was greater than 90 weight %, the major impurity being the corresponding $^-C(SO_2CF_3)_2(SO_2F)$ salt. The product was also characterized for melting point (T_m) according to Test Method I and for onset of thermal decomposition (T_d) according

20   to Test Method II. Results are shown in Table 4.

Antistat 20

Synthesis of Trimethyl-2-acetoxyethylammonium bis(trifluoromethylsulfonyl)imide, $(CH_3)_3N^+CH_2CH_2OC(O)CH3 \ ^-N(SO_2CF_3)_2$

25   Acetylcholine chloride (98g, Research Organics, Cleveland, OH) and $LiN(SO_2CF_3)_2$ (HQ-115) (165.8g) were combined in 600mL of water with magnetic stirring. A viscous, immiscible oil separated as a lower liquid phase. The resulting mixture was worked up essentially as described for Antistat 16, except that the ionic liquid product was not completely miscible with methylene chloride,

30   forming 3 separate liquid phases in the presence of water. The lower ionic liquid phase and the middle CH_2Cl_2 phase were both carried through the workup. After vacuum stripping all volatiles, a total of 179.1g (77% yield) of colorless oil product

of high purity was obtained, which was identified as the title compound by ^{1}H, ^{13}C and ^{19}F NMR. The product was also characterized for melting point (T_m) according to Test Method I and for onset of thermal decomposition (T_d) according to Test Method II. Results are shown in Table 4.

5

Antistat 21

Synthesis of Trimethyl-2-hydroxyethylammonium bis(perfluorobutanesulfonyl)imide, $(CH_3)_3N^+CH_2CH_2OH$ $^-N(SO_2C_4F_9)_2$

10   Choline chloride (37.34g) and $LiN(SO_2C_4F_9)_2$ (142.7g, prepared essentially according to Example 4 in U.S. Patent No. 5,874,616 (Howells et al.) were combined in 400mL of water with magnetic stirring. A viscous, immiscible oil separated as a lower liquid phase. The mixture was transferred to a separatory funnel, and 110mL of diethyl ether were added. The mixture was shaken

15 vigorously and allowed to phase separate. The lower organic phase was isolated and washed with two additional 400mL portions of water. The washed ether phase was isolated and vacuum stripped at 30-100°C , 20 - 10^{-3} Torr to remove all volatiles. The resulting colorless oil product (155.3g, 93% yield) of high purity was obtained, which was identified as the title compound by ^{1}H, ^{13}C and ^{19}F NMR. The

20 product was also characterized for melting point (T_m) according to Test Method I and for onset of thermal decomposition (T_d) according to Test Method II. Results are shown in Table 4.

Antistat 22

25   Larostat™ HTS 905A, octyldimethylhydroxyethylammonium methanesulfonate ($C_8H_{17}N^+(CH_3)_2C_2H_4OH$ $^-OSO_2CH_3$) was also characterized for melting point (T_m) according to Test Method I and for onset of thermal decomposition (T_d) according to Test Method II. Results are shown in Table 4.

Table 4. Melting Point (T_m) and Onset of Thermal Decomposition (T_d) Values

Antistat	Formula	T_m (°C)	T_d (°C)
16	$C_8H_{17}N^+(CH_3)_2CH_2CH_2OH$ $^-N(SO_2CF_3)_2$	None detected	409
17	$C_8H_{17}N^+(CH_3)_2CH_2CH_2OH$ $^-OSO_2C_4F_9$	147	374
18	$C_8H_{17}N^+(CH_3)_2CH_2CH_2OH$ $^-OSO_2CF_3$	-26	370
19	$C_8H_{17}N^+(CH_3)_2CH_2CH_2OH$ $^-C(SO_2CF_3)_3$	None detected	387
20	$(CH_3)_3N^+CH_2CH_2OC(O)CH3$ $^-N(SO_2CF_3)_2$	24	361
21	$(CH_3)_3N^+CH_2CH_2OH$ $^-N(SO_2C_4F_9)_2$	32	402
22	$C_8H_{17}N^+(CH_3)_2CH_2CH_2OH$ $^-OSO_2CH_3$	About 30	289

The results in Table 4 show that among antistats having the same cation, those containing weakly coordinating fluoroorganic anions (Antistats 16-21) exhibited greatly increased thermal stability relative to that of Antistat 22, which has a more strongly coordinating anion.

Antistat 23

Aliquat™ 336, methyltrioctylammonium chloride $((C_8H_{17})_3N^+(CH_3)$ $Cl^-)$, a liquid at room temperature, was characterized for onset of thermal decomposition (T_d) according to Test Method II. Results are shown in Table 1.

Antistat 24

Synthesis of tetrabutylphosphonium perfluorobutanesulfonate, $(C_4H_9)_4P^+$ $^-OSO_2C_4F_9$

This compound can be prepared as follows: Potassium perfluorobutanesulfonate is prepared essentially as in Example 3 of U.S. Patent No. 2,732,398 (Brice et al.), except that PBSF is substituted for $CF_3(CF_2)_4SO_2F$. The potassium ion is exchanged for a proton using an ion exchange column

-48-

(Amberjet™ 1200 H, available from Sigma-Aldrich, Milwaukee, WI.). The resulting perfluorobutanesulfonic acid is combined with an equal molar amount of tetrabutylphosphonium hydroxide (available from Sigma-Aldrich, Milwaukee, WI.) in an acid-base reaction, resulting in a high yield and high purity

5   tetrabutylphosphonium perfluorobutanesulfonate.

PREPARATION OF REPELLENT ADDITIVES

Fluorochemical Repellent FR-1

Fluorochemical Repellent FR-1 (a fluorochemical oxazolidinone) was

10   prepared by reacting N-methylperfluorooctylsulfonamide with epichlorohydrin to form the fluorochemical chlorohydrin, $C_8F_{17}SO_2N(Me)CH(OH)CH_2Cl$, which was further reacted with octadecyl isocyanate at a 1:1 molar ratio followed by ring closure using essentially the same procedure as described in Scheme I of U.S. Patent No. 5,025,052 (Crater et al.).

15

Fluorochemical Repellent FR-2

Fluorochemical Repellent FR-2 (a fluorochemical ester) was prepared by esterifying MeFOSE alcohol with Empol™ 1008 dimer acid at a molar ratio of 2:1 using the following procedure. A 500 mL 2-necked round-bottom flask equipped

20   with overhead condenser, thermometer and Dean-Stark trap wrapped with heat tape was charged with 57.8 g (0.190 eq) of Empol™ 1008 dimer acid, 100 g (0.185 eq) of MeFOSE alcohol, 1 g of p-toluenesulfonic acid and 50 g of toluene. The resulting mixture was placed in an oil bath heated to 150°C. The degree of esterification was monitored by measuring the amount of water collected in the

25   Dean-Stark trap and also by using gas chromatography to determine the amount of unreacted fluorochemical alcohol. After 18 hours of reaction, about 2.8 mL of water was collected and a negligible amount of fluorochemical alcohol remained, indicating a complete reaction. The reaction mixture was then cooled to 100°C and was twice washed with 120 g aliquots of deionized water, the final water wash

30   having a pH of 3. The final wash was removed from the flask by suction, and the reaction mixture was heated to 120°C at an absolute pressure of about 90 torr to

remove volatiles. The resulting product, a brownish solid, was characterized as containing the desired fluorochemical ester by ^{1}H and ^{13}C NMR spectroscopy and thermogravimetric analysis.

5   **Fluorochemical Repellent FR-3**

Fluorochemical Repellent FR-3 (a fluorochemical ester) was prepared by esterifying MeFOSE alcohol with Pripol™ 1048 dimer/trimer acid at a molar ratio of 2:1 using essentially the same procedure as was used for preparing Fluorochemical Repellent FR-2.

10

Fluorochemical Repellent FR-4

Fluorochemical Repellent FR-4 (a fluorochemical ester) was prepared by esterifying MeFOSE alcohol with dodecanedioic acid at a molar ratio of 2:1 using essentially the same procedure as was used for preparing Fluorochemical Repellent

15   FR-2.

Example 1

Fluorochemical Repellent FR-1 and HTS-905 (Antistat 22) were dry blended with a mixture of polybutylene PB0200 and polypropylene PP3505 400

20   melt flow resin (in a weight ratio of 1 part PB0200 to 10 parts PP3505) at 0.85 and 1 weight % of the polypropylene resin, respectively. The mixture was extruded, on a 1.9 cm Brabender extruder with a 25.4 cm die, into blown microfibers with a diameter of less than about 10 microns (Wente, Van A., "superfine Thermoplastic fibers", Industrial and Eng. Chemistry, Vol. 48, No. 8, 1956, pp. 1342-1345, and

25   Naval Research Laboratory Report 111437, April 15, 1954). The first extruder zone was set at 265°C, and all other zones were set at 275°C. The die air temperature was set at 277°C, and the melt temperature was recorded at 279°C. The metering gear pump speed was set at 70 rpm. The die was configured with an air gap setting of 0.763 mm and a set back of 0.69 mm. With a collector distance

30   of 30.5 cm, the take up speed was set to deliver a melt blown nonwoven formed from the microfibers with a basis weight of 50 grams/m^2. The resulting nonwoven samples were calendered on a 5% bond area embossing roll at 93.3 °C at 30.5

cm/min. and at 35.7 Kg/lineal cm. The nonwoven samples were tested for oil and water repellency according to Test Methods V and VI. The nonwoven samples were also conditioned at 50% relative humidity (23°C) and tested for static charge dissipation according to Test Method III. Results are shown in Table 5.

Comparative Example C1

Nonwoven samples were made and tested essentially as in Example 1, except that no HTS-905 was used. The results are shown in Table 5.

Comparative Example C2

Nonwoven samples were made and tested essentially as in Example 1, except that no repellent was used, and the level of HTS-905 was 0.5 weight % of the polypropylene resin. The results are shown in Table 5.

Table 5. Repellency and Static Charge Dissipation Properties of Polypropylene Melt-Blown Nonwovens

Example No.	Repel-lent (Wt %)	Antistat (Wt %)	Repel-lency		Static Decay (sec)
			O	W	
1	FR-1 (0.85%)	Antistat 22 (1%)	6	10	0.07
C1	FR-1 (0.85%)	None	6	10	>100.0
C2	None	Antistat 22 (1%)	0	3	0.01

O = oil

W = water

The results in Table 5 show that the combination of repellent and ionic antistat compound in a thermoplastic polymer provided excellent static charge dissipation and excellent repellency properties.

5 **Examples 2-6 and Comparative Example C3**

Fluorochemical Repellent FR-1 and Antistat 15 $C_{12}H_{25}$-cyc-$[N^{+}C_2H_4N(CH_2CH_2OH)C]C_2H_5$ $^{-}OSO_2C_6H_4CH_3$) were dry blended with PP3505. FR-1 was used at 1 weight % based on the weight of PP3505, and Antistat 15 was used at 0.5, 0.6, 0.7, 0.8, and 1 weight %, also 10 based on the weight of PP3505. Nonwoven samples were made and tested essentially as in Example 1. For comparison purposes, nonwoven samples were made and tested essentially as in Example 1 without repellent or antistat (Comparative Example C3). The results are shown in Table 6.

15 **Example 7**

Fluorochemical Repellent FR-1 (1 weight %) and Antistat 15 (1 weight %) were dry blended with a mixture of PP3505 (80 weight %) and PB8340 (20 weight %). Nonwoven samples were made and tested essentially as in Example 1, and the results are shown in Table 6.

20

Table 6. Repellency and Static Charge Dissipation Properties of

Polypropylene Melt-Blown Nonwovens

Example No.	Repellent FR-1 (weight %)	Antistat 15 (weight %)	Repellency		Static Decay (sec)
			Oil	Water	
C3	0	0	0	2	WNC[1]
2	1.0	0.5	3	8	0.15
3	1.0	0.6	3	8	0.11
4	1.0	0.7	2	8	0.06
5	1.0	0.8	2	8	0.09
6	1.0	1.0	2	8	0.04
7	1.0	1.0	4	9	0.05

[1] Will not accept charge, therefore not antistatic.

The results in Table 6 show that a combination of a fluorochemical oxazolidinone and Antistat 15 (imidazolinium toluenesulfonate ionic antistat) provided both repellency and good static charge dissipation properties in polypropylene, and that these properties were further enhanced with added polybutylene.

Example 8

Fluorochemical Repellent FR-1 (0.85 weight %) and antistat HTS-904 (1 weight %) were dry blended with PP3505. Nonwoven samples were made from this blend and tested essentially as in Example 1. The results are shown in Table 7.

Example 9

Fluorochemical Repellent FR-1 (0.85 weight %) and antistat HTS-904 (1 weight %) were dry blended with a mixture of PP3503 (85 weight %) and PB8340 (15 weight %). Nonwoven samples were made from this blend and tested essentially as in Example 1. The results are shown in Table 7.

Table 7. Repellency and Static Charge Dissipation Properties of

Polypropylene Melt-Blown Nonwovens

Example No.	PB8340 (Wt %)	Repellent (wt %)	Antistat (Wt %)	Repellency		Static Decay (sec)
				O	W	
8	0	FR-1 (0.85%)	HTS-904 (1%)	2	9	0.01
9	15	FR-1 (0.85%)	HTS-904 (1%)	6	10	0.05

O = oil

W = water

The results in Table 7 show that the addition of polybutylene significantly increased the repellency of a polypropylene nonwoven containing a combination of a fluorochemical repellent and an antistat, without loss of excellent antistatic properties.

Comparative Examples C4-C6

Nonwoven samples containing 0 or 1.0 weight % Fluorochemical Repellent FR-1 and 0, 1.0, or 1.25 weight % Anstex™ SA-300 nonionic antistat were prepared and tested essentially as in Example 1. The results are shown in Table 8.

Table 8. Repellency and Static Charge Dissipation Properties of

Polypropylene Melt-Blown Nonwovens

Example No.	Repellent FR-1 (wt. %)	Antistat SA-300 (wt. %)	Repellency		Static Decay (sec)
			Oil	Water	
C3	0	1.0	0	2	14.9
C4	1.0	0.0	4	9	WNC[1]
C5	1.0	1.25	4	8	WNC[1]

[1] Will not accept charge, therefore not antistatic.

The results in Table 8 show that a loss of antistatic properties was obtained when a nonionic antistat was used in combination with a repellent.

Examples 10-19 and Comparative Examples C7-C17

Antistats 16-19 and 22 along with 1 or 1.25 weight % Fluorochemical Repellent FR-1, FR-2, FR-3, or FR-4 were incorporated into polypropylene melt blown fibers, which were processed into nonwoven fabrics according to the melt-blown extrusion procedure described in U.S. Patent No. 5,300,357 (Gardiner), column 10. For comparison, polypropylene melt blown fibers without repellent or antistat, and with an Antistat but without a repellent were made and formed into nonwoven fabrics by essentially the same process. For additional comparison, polypropylene melt blown fibers with only Fluorochemical Repellents FR-1, FR-2, FR-3, or FR-4 were made and processed into nonwoven fabrics by essentially the same process. The extruder used was a Brabender 42 mm conical twin screw extruder, with maximum extrusion temperature of 270-280°C and distance to the collector of 12 inches (30 cm).

Antistat, Fluorochemical Repellent, and Escorene ™ PP3505 polypropylene were mixed by blending in a paperboard container using a mixer head affixed to a hand drill for about one minute until a visually homogeneous mixture is obtained. The Antistat and Fluorochemical Repellent were dispersed in the molten polypropylene by mixing in the melt extrusion apparatus just prior to melt blowing.

Except as noted, the weight percent of the compound in the polypropylene was about 1%.

The process condition for each mixture was the same, including the melt blowing die construction used to blow the microfiber web, the basis weight of the web (50±5 g/m^2) and the diameter of the microfibers (5-18 micrometers). Unless otherwise stated, the extrusion temperature was 270-280°C, the primary air temperature was 270°C, the pressure was 124 kPa (18 psi), with a 0.076 cm air gap width, and the polymer throughput rate was about 180 g/hr/cm.

The resulting melt blown polypropylene fabrics were evaluated for antistatic performance, oil repellency, and water repellency using Test Methods III, V, and VI. The results are shown in Tables 9 and 10.

Table 9. Static Charge Dissipation, Oil Repellency, and Water Repellency of Escorene ™ PP3505 Polypropylene Nonwovens

Ex. No.	Repel-lent (Wt %)	Antista t (Wt %)	Repel-lency		Charge (Kvolts)			Static Decay (sec)		
			0	W	10% RH	25% RH	50% RH	10% RH	25% RH	50% RH
C6	None	None	0	2	4.3	5+ 1.7 5	5+ 1.7 5	60+	60 >10 >10	60 >10 >10
C7	FR-1 1%	None	1	8	WNC	WNC	WNC	WNC	WNC	WN C
C8	FR-2 1%	None	0	7	NR	NR	NR	NR	NR	NR
C9	FR-3 1.25 %	None	0	7	NR	NR	-.5	NR	NR	>10
C10	FR-4 1%	None	1	7	NR	NR	-.75	NR	NR	>10

RH = relative humidity

WNC = will not accept charge (therefore not antistatic)

NR = not run

O = oil

W = water

The results in Table 9 show that polypropylene nonwoven alone lacked oil and water repellency and antistatic properties, and that the addition of fluorochemical repellents significantly increased repellency, particularly the water repellency of polypropylene, but made no contribution to improvement of antistatic properties.

Table 10. Static Charge Dissipation, Oil Repellency, and Water Repellency of Escorene ™ PP3505 Polypropylene Nonwovens

Ex. No.	Repel-lent (Wt %)	Antistat (Wt %)	Repel-lency		Charge (Kvolts)			Static Decay (sec)		
			0	W	10% RH	25% RH	50% RH	10% RH	25% RH	50% RH
C12	None	Antistat 22 (1%)	0	2	5+	3.4	5+	0.86	0.14	0.03
10	FR-1 (1%)	Antistat 22 (1%)	2	9	5	5	5	0.6	0.3	0.03
11	FR-2 (1%)	Antistat 22 (1%)	1	7	5	5	4	0.7	0.3	0.05
12	FR-4 (1%)	Antistat 22 (1%)	1	5	5	5	4	1.3	1.1	0.4
C13	None	Antistat 16 (1%)	0	2	5+	5+	5+	0.14	0.19	0.63
13	FR-1 (1%)	Antistat 16 (1%)	1.5	9	5	5	5	0.5	0.2	0.2
14	FR-3 (1.25%)	Antistat 16 (1%)	1	7	4	4.7	4.5	0.1	0.09	0.1
15	FR-4 (1%)	Antistat 16 (1%)	0	5	4	4.5	4.7	0.6	0.2	2.8
C14	None	Antistat 16 (0.5%)	0	2	NR	5	5	NR	>10	0.95
16	FR-1 (1%)	Antistat 16 (0.5%)	1	7	5	5	5	0.5	0.2	0.2
C15	None	Antistat 17 (1%)	0.5	2	5	5	5	0.90	0.02	0.02
17	FR-1 (1%)	Antistat 17 (1%)	1	8	4.2	4.6	5	8.8	7.3	1.4
C16	None	Antistat 18 (1%)	0	2	5	5	5	4.17	0.09	0.03
18	FR-1	Antistat 18	2	9	5	5	5	0.2	0.1	0.04

Ex. No.	Repel-lent (Wt %)	Antistat (Wt %)	Repel-lency		Charge (Kvolts)			Static Decay (sec)		
			0	W	10% RH	25% RH	50% RH	10% RH	25% RH	50% RH
	(1%)	(1%)								
C17	None	Antistat 19 (1%)	0	2	NR	NR	5	NR	NR	>10
19	FR-1 (1%)	Antistat 19 (1%)	2	9	5	5	5	0.3	0.1	0.2

RH = relative humidity

NR = not run

O = oil

W = water

The results in Table 10 together with those in Table 9 show that the presence of a combination of a fluorochemical repellent and an octyldimethyl-2-hydroxyethylammonium antistat produced excellent antistatic properties with repellency essentially the same as when repellent was used alone, and, in some cases, improved the antistatic properties compared with those found when the antistat was used alone.

Examples 20-26 and Comparative Examples C18-C23

Antistats 1-4, 20, and 21 alone and in combination with 1 or 1.25 weight % Fluorochemical Repellent FR-1 or FR-3 were incorporated into polypropylene melt blown fibers and processed into nonwoven fabrics essentially as in Examples 10-19 and Comparative Examples C12-C17. The resulting melt blown polypropylene fabrics were evaluated for antistatic performance, oil repellency, and water repellency using Test Methods III, V, and VI. The results are shown in Table 11.

Table 11. Static Charge Dissipation, Oil Repellency, and Water Repellency of
Escorene ™ PP3505 Polypropylene Nonwovens

Ex. No.	Repel- lent (wt %)	Antistat (wt %)	Repel- lency		Charge (Kvolts)			Static Decay (sec)		
			O	W	10% RH	25% RH	50% RH	10% RH	25% RH	50% RH
C18	None	Antistat 20 (1%)	0	2	NR	5+	5+	NR	>60	>60
20	FR-1 (1%)	Antistat 20 (1%)	1	8	5+	5+	5+	0.01	0.03	0.9
21	FR-3 (1.25%)	Antistat 20 (1%)	1	8	NR	5+	4.4	NR	0.02	0.06
C19	None	Antistat 21 (1%)	0	2	NR	4.8	5+	NR	56	>60
22	FR-1 (1%)	Antistat 21 (1%)	1.5	9	NR	5+	5+	NR	>60	0.9
C20	None	Antistat 1 (1%)	0	2	5	5	5	0.03	0.03	0.02
23	FR-1 (1%)	Antistat 1 (1%)	1	9	NR	2.5	2.5	NR	>10	0.01
C21	None	Antistat 2 (1%)	0	2	NR	NR	5	NR	NR	>10
24	FR-1 (1%)	Antistat 2 (1%)	2	9	NR	NR	-1.5	NR	NR	>10
C22	None	Antistat 3 (1%)	0	2	NR	NR	5	NR	NR	>10
25	FR-1 (1%)	Antistat 3 (1%)	2	9	NR	0.7	1.5	NR	>10	0.01
C23	None	Antistat 4 (1%)	0	2	NR	3.7	3.6	NR	60	60
26	FR-1 (1%)	Antistat 4 (1%)	1	8	NR	4	4.2	NR	2.8	11

RH = relative humidity

NR = not run

O = oil

W = water

The results in Table 11 together with those in Table 9 show that the

5   combination of fluorochemical repellent and an alkyl ammonium antistat provided

essentially the same or better repellency compared with the repellency obtained

when the repellent was used alone. Furthermore, the combination of

fluorochemical repellent and antistat often provided significantly improved

antistatic properties.

10

Examples 27-34 and Comparative Examples C24-C28

Antistats 5-9 alone and in combination with 1 or 1.25 weight %

Fluorochemical Repellent FR-1 or FR-3 were incorporated into polypropylene melt

blown fibers and processed into nonwoven fabrics essentially as in Examples 10-19

15   and Comparative Examples C12-C17. The resulting melt blown polypropylene

fabrics were evaluated for antistatic performance, oil repellency, and water

repellency using Test Methods III, V, and VI. The results are shown in Table 12.

Table 12. Static Charge Dissipation, Oil Repellency, and Water Repellency of Escorene ™ PP3505 Polypropylene Nonwovens

Ex. No.	Repellent (wt %)	Antistat (wt %)	Repellency		Charge (Kvolts)			Decay Rate (sec)		
			O	W	10% RH	25% RH	50% RH	10% RH	25% RH	50% RH
C24	None	Antistat 5 (1%)	0	2	4.8	4.7	5+	34	8.9	45
27	FR-1 (1%)	Antistat 5 (1%)	1	6	5+	5+	5+	1.3	0.7	1.1
28	FR-3 (1.25%)	Antistat 5 (1%)	0.5	6	5+	5+	5+	0.4	1.3	0.6
C25	None	Antistat 6 (1%)	0	2	NR	5+	5+	NR	56	1.01
29	FR-1 (1%)	Antistat 6 (1%)	1	7	NR	2.7	4.7	NR	5	21
30	FR-3 (1.25%)	Antistat 6 (1%)	1	6	NR	1.3	4.2	NR	0.01	33
C26	None	Antistat 7 (1%)	0	2	NR	3.6	5+	NR	>60	3.98
31	FR-1 (1%)	Antistat 7 (1%)	1	7	NR	4.3	5+	NR	>60	9.9
32	FR-3 (1.25%)	Antistat 7 (1%)	1	6	NR	4.2	5+	NR	36	9.9
C27	None	Antistat 8 (1%)	0	2	NR	5+	4.3	NR	49	0.06
33	FR-1 (1%)	Antistat 8 (1%)	1.5	9	NR	5+	5+	NR	>60	1.5
C28	None	Antistat 9 (1%)	0	2	NR	5+	5+	NR	>60	0.46
34	FR-1 (1%)	Antistat 9 (1%)	2	10	NR	5+	5+	NR	>60	0.5

RH = relative humidity

NR = not run

O = oil

W = water

The results in Table 12 together with those in Table 9 show that the combination of fluorochemical repellent and alkyl pyridinium antistat provided essentially the same or better repellency compared with the repellency found when the repellent was used alone. Furthermore, the combination of repellent and

5   antistatic compound provided significantly improved antistatic properties in some instances.

Examples 35-38 and Comparative Examples C29-C32

Antistats 10-14 alone and in combination with 1 weight % Fluorochemical

10   Repellent FR-1 were incorporated into polypropylene melt blown fibers and processed into nonwoven fabrics essentially as in Examples 10-19 and Comparative Examples C12-C17. The resulting melt blown polypropylene fabrics were evaluated for antistatic performance, oil repellency, and water repellency using Test Methods III, V, and VI. The results are shown in Table 13.

Table 13. Static Charge Dissipation, Oil Repellency, and Water Repellency of
Escorene ™ PP3505 Polypropylene Nonwovens

Ex. No.	Repel-lent (wt %)	Antistat (wt %)	Repel-lency		Charge (Kvolts)			Decay Rate (sec)		
			O	W	10% RH	25% RH	50% RH	10% RH	25% RH	50% RH
C29	None	Antistat 10 (1%)	0	2	4.1	3.9	3.4	60+	0.01	53
35	FR-1 (1%)	Antistat 10 (1%)	2	8	4.7	5	5+	0.01	0.02	0.03
C30	None	Antistat 11 (1%)	0	2	5+	5+	5+	0.02	20	0.03
36	FR-1 (1%)	Antistat 11 (1%)	1.5	8	5+	5+	5+	0.7	0.04	0.03
C31	None	Antistat 13 (1%)	0	2	4.5	4.9	4.2	>60	>60	>60
37	FR-1 (1%)	Antistat 13 (1%)	1	8	4.5	5+	5+	0.10	0.02	0.10
C32	None	Antistat 14 (1%)	0	2	NR	3.8	4.4	NR	>60	>60
38	FR-1 (1%)	Antistat 14 (1%)	1	8	4	3.7	3.6	1.8	0.02	0.01

RH = relative humidity

NR = not run

O = oil

W = water

The results in Table 13 together with those in Table 9 show that the
combination of repellent and imidazolium antistat provided essentially the same or
better repellency compared with the repellency found when the repellent was used
alone. Furthermore, the combination of repellent and antistat provided
significantly improved antistatic properties.

Example 39 and Comparative Example C33

Antistat 24 alone and in combination with 1 weight % Fluorochemical
Repellent FR-1 was incorporated into polypropylene melt blown fibers and
processed into nonwoven fabrics essentially as in Examples 10-19 and
5   Comparative Examples C12-C17. The resulting melt blown polypropylene fabrics
were evaluated for antistatic performance, oil repellency, and water repellency
using Test Methods III, V, and VI. The results are shown in Table 14.

Table 14. Static Charge Dissipation, Oil Repellency, and Water Repellency of
10   Escorene ™ PP3505

Polypropylene Nonwovens

Ex. No.	Repellent (wt %)	Antistat (wt %)	Repellency		Charge (Kvolts)			Decay Rate (sec)		
			O	W	10% RH	25% RH	50% RH	10% RH	25% RH	50% RH
C33	None	Antistat 24 (1%)	0	2	NR	5+	5+	NR	25	12
39	FR-1 (1%)	Antistat 24 (1%)	3	9	5	4.9	4.3	0.5	0.4	0.6

O = oil

W = water

RH = relative humidity

15   NR = not run

The results in Table 14 together with those in Table 9 show that the
combination of repellent and phosphonium antistat provided essentially the same
or better repellency compared with the repellency found when the repellent was
20   used alone. Furthermore, the combination of repellent and antistat provided
significantly improved antistatic properties.

Example 40 and Comparative Example C34

Lithium perfluorobutanesulfonate alone and in combination with 1 weight % Fluorochemical Repellent FR-1 was incorporated into polypropylene melt blown fibers and processed into nonwoven fabrics essentially as in Examples 10-19 and

5   Comparative Examples C12-C17. The resulting melt blown polypropylene fabrics were evaluated for antistatic performance, oil repellency, and water repellency using Test Methods III, V, and VI. The results are shown in Table 15.

Table 15. Static Charge Dissipation, Oil Repellency, and Water Repellency of

10   **Escorene ™ PP3505 Polypropylene Nonwoven**

Ex. No.	Repel-lent (Wt %)	Antistat (Wt %)	Repel-lency		Charge (Kvolts)			Decay Rate (sec)		
			O	W	10% RH	25% RH	50% RH	10% RH	25% RH	50% RH
C34	None	Li+ -OSO$_2$C$_4$F$_9$	0	2	NR	NR	5	NR	NR	0
40	FR-1	Li+ -OSO$_2$C$_4$F$_9$	1	6	NR	NR	5	NR	NR	0.03

O = oil

W = water

RH = relative humidity

NR = not run

15

The results in Table 15 together with those in Table 9 show that the combination of repellent and lithium perfluorobutanesulfonate antistat provided essentially the same repellency as that found when the repellent was used alone. Furthermore, the combination of repellent and antistat provided essentially the

20   same antistatic properties as that found when the antistat was used alone.

Comparative Examples C35-C43

Aluminum stearate, lithium stearate, and glycerol monostearate in combination with 1 weight % Fluorochemical Repellent FR-1, FR-2, or FR-4 was

25   incorporated into polypropylene melt blown fibers and processed into nonwoven fabrics essentially as in Examples 10-19 and Comparative Examples C12-C17.

The resulting melt blown polypropylene fabrics were evaluated for antistatic performance, oil repellency, and water repellency using Test Methods III, V, and VI. The results are shown in Table 16.

Table 16. Static Charge Dissipation, Oil Repellency, and Water Repellency of Escorene ™ PP3505

Polypropylene Nonwoven

Ex. No.	Repellent (Wt %)	Antistat (Wt %)	Repellency		Charge (Kvolts)		Decay Rate (sec)	
			O	W	25% RH	50% RH	25% RH	50% RH
C35	FR-1 (1%)	AlOCO(CH$_2$)$_{16}$CH$_3$ (1%)	0	9	NR	-1	NR	>10
C36	FR-1 (1%)	LiOCO(CH$_2$)$_{16}$CH$_3$ (1%)	1	9	NR	2.4	NR	>10
C37	FR-1 (1%)	HOCH2CH(OH)CH2O-CO(CH$_2$)$_{16}$CH$_3$ (1%)	1	9	1.2	0.9	0	>10
C38	FR-2 (1%)	AlOCO(CH$_2$)$_{16}$CH$_3$ (1%)	2	8	NR	2	NR	>10
C39	FR-2 (1%)	LiOCO(CH$_2$)$_{16}$CH$_3$ (1%)	1	8	NR	-0.5	NR	>10
C40	FR-2 (1%)	HOCH2CH(OH)CH2O-CO(CH$_2$)$_{16}$CH$_3$ (1%)	0	5	NR	2	NR	>10
C41	FR-4 (1%)	AlOCO(CH$_2$)$_{16}$CH$_3$ (1%)	1	9	NR	0.5	NR	>10
C42	FR-4 (1%)	LiOCO(CH$_2$)$_{16}$CH$_3$ (1%)	2	6	NR	-0.9	NR	>10
C43	FR-4 (1%)	HOCH2CH(OH)CH2O-CO(CH$_2$)$_{16}$CH$_3$ (1%)	2	8	NR	2.2	NR	>10

RH = relative humidity

NR = not run

O = oil

W = water

The results in Table 16 show that neither the nonionic antistatic compounds nor the ionic antistatic compounds (that lack an anion for which the conjugate acid is a strong acid) provided antistatic properties in combination with fluorochemical repellents.

Example 41 and Comparative Examples C44-C46

Antistat 16, $C_8H_{17}N^+(CH_3)_2C_2H_4OH$ $^-N(SO_2CF_3)_2$ (2 weight %) and Fluorochemical Repellent FR-1 (2 weight %) were incorporated into MORTHANE™ PS440-200 urethane melt blown fibers, which were made and processed into a nonwoven fabric essentially as described in Examples 10-19, except that the extrusion temperature was 230°C. For comparisons, MORTHANE™ PS440-200 urethane melt blown fibers without antistat or repellent, with Antistat 16 (2 weight %) alone, and with Fluorochemical Repellent FR-1 (2 weight %) alone were made and processed into nonwoven fabrics essentially as described in Comparative Examples C7-C17. The resulting fabrics were tested for antistatic performance, oil repellency, and water repellency, using Test Methods III, V, and VI. The results are shown in Table 17.

Table 17. Static Charge Dissipation, Oil Repellency, and Water Repellency of Melt Blown MORTHANE™ PS440-200 Urethane Nonwoven Fabrics

Ex. No.	Repel- lent (Wt %)	Antistat (Wt %)	Repel- lency		Charge (Kvolts)			Decay Rate (sec)		
			O	W	10% RH	25% RH	50% RH	10% RH	25% RH	50% RH
C44	None	None	0	2	NR	5	5	NR	>60	>60
C45	None	Antistat 16 (2%)	0	2	5	5	5	0.09	0.08	0.08
C46	FR-1 (2%)	None	6	4	5	5	5	4.20	3.34	2.4
41	FR-1 (2%)	Antistat 16 (2%)	6	7	5	5	5	0.08	0.06	0.07

RH = relative humidity

NR = not run

O = oil

W = water

The results in Table 17 show that the combination of fluorochemical
repellent and ionic antistat provided both very good repellency and good antistatic
properties in polyurethane nonwoven fabric.

Example 42 and Comparative Example C47-49

Antistat 16 (1 weight %) and Fluorochemnical Repellent FR-1 (1 weight %)
were incorporated into ASPUN™ 6806 poly(ethylene/octene) melt blown fibers,
which were made and processed into a nonwoven fabric essentially as described in
Examples 10-19, except that the extrusion temperature was 240°C. For
comparisons, ASPUN™ 6806 melt blown fibers without any antistat or repellent,
with Antistat 16 (1 weight %) alone, and with Fluorochemical Repellent FR-1 (1
weight %) alone were made and processed into nonwoven fabrics essentially as
described in Comparative Examples C7-C17. The resulting fabrics were tested for
antistatic performance, oil repellency, and water repellency, using Test Methods III,
V, and VI. The results are shown in Table 18.

Table 18. Static Charge Dissipation, Oil Repellency, and Water Repellency of
Melt Blown ASPUN™ 6806 Poly(ethylene/octene) Nonwoven Fabrics

Ex. No.	Repel-lent (Wt %)	Antistat (Wt %)	Repel-lency		Charge (Kvolts)			Decay Rate (sec)		
			O	W	10% RH	25% RH	50% RH	10% RH	25% RH	50% RH
C47	None	None	0	2	NR	NR	3	NR	NR	>60
C48	None	Antistat 16 (1%)	0	2	5	5	5	0.07	0.08	0.07
C49	FR-1 (1%)	None	3	9	NR	1.7	3	NR	0.00	7.68
42	FR-1 (1%)	Antistat 16 (1%)	6	7	5	5	5	0.02	0.01	0.01

RH = relative humidity

NR = not run

O = oil

W = water

The results in Table 18 show that the combination of fluorochemical repellent and ionic antistat provided both very good repellency and excellent antistatic properties in poly(ethylene/octene) nonwoven fabric.

Examples 43-45 and Comparative Example 50

Polypropylene films containing tetrabutylphosphonium perfluorobutanesulfonate (Antistat 24) and Fluorochemical Repellent FR-1, FR-3, or FR-4 were prepared and evaluated for repellency and antistatic performance. For comparison, a polypropylene film without antistat or repellent was essentially identically prepared and evaluated. The melt-blown nonwoven fabrics of Example 39, and Comparative Example 7, as well as nonwoven fabrics made essentially identically to Example 39 but with FR-3 and FR-4 substituted for FR-1 were pressed into films as follows: About 3.4 g of the folded melt-blown fabric was placed on a steel plate within the perimeter of an 11.2 cm by 17.1 cm by 0.177 mm thick shim and covered with another steel plate. This assembly was then placed on a platen press heated to 200°C, with the platens nearly touching, for about 30 seconds to pre-melt the fabric and allow for escape of air before pressing. Next, the construction was placed under 0.91 metric ton of pressure for about one minute. The assembly was removed from the press and allowed to cool for about 30 seconds between two unheated platens. The formed film was then removed from the shim and steel plates.

The resulting films were evaluated for antistatic performance, oil repellency, and water repellency using Test Methods III, V, and VI. The results are shown in Table 19.

Table 19. Static Charge Dissipation, Oil Repellency, and Water Repellency of

Escorene ™ PP3505

Polypropylene Films

Ex. No.	Repel-lent (Wt %)	Antistat (Wt %)	Repel-lency		Charge (Kvolts)			Decay Rate (sec)		
			O	W	10% RH	25% RH	50% RH	10% RH	25% RH	50% RH
C50	None	None	0	4	NR	NR	1.5	NR	NR	>10
43	FR-1 (1%)	Antistat 24 (1%)	2	10	NR	5	5	NR	>10	1.3
44	FR-3 (1%)	Antistat 24 (1%)	1	8	5	5	4.3	>10	2.1	0.7
45	FR-4 (1%)	Antistat 24 (1%)	1	4	5	5	4.2	4.4	1.6	0.02

RH = relative humidity

NR = not run

O = oil

W = water

The results in Table 19 show that the combination of fluorochemical
repellent and phosphonium antistat provided both good repellency and good
antistatic properties in polypropylene films.

Examples 46-49 and Comparative Examples C51-56

A polypropylene nonwoven fabric, having a basis weight of 220 grams/m^2,
was made essentially as Comparative Example 7, but using Montell™ H442PP
(polypropylene) with the collector speed adjusted for this basis weight. The
resulting fabric was tested for oil repellency, water repellency, and antistatic
performance (Test Methods V, VI, and III) before and after topical treatment with a
repellent, various ionic antistats, and combinations of the repellent and antistats.
Pad bath solutions (500 grams) made up of 80 weight % water and 20 weight %
isopropanol (IPA) without and with 0.366 weight % repellent (9.15 grams of 20

weight % solids FC-808 diluted to 500 grams with the 80/20 water IPA), with
0.366 weight % antistat, and with combinations of 0.366 weight % repellent and
0.366 weight % antistat were prepared. A weighed (4-6 grams) piece of nonwoven
fabric was dipped in each pad bath and passed between two 12.7 cm rubber rolls at

5   a pressure of 0.41 MPa and a speed of 7.6 m/min. The wet fabric was weighed and
then dried in a forced air oven at 149°C for five minutes. The target amount of
repellent and antistat applied to the fabric was 0.55 weight %. The actual amount
ranged from 0.51 to 0.64 %. Repellency and antistatic properties of the topically
treated nonwoven fabric are shown in Table 20.

10

Table 20. Static Charge Dissipation, Oil Repellency, and Water Repellency of

Topically Treated

Polypropylene Nonwovens

Ex. No.	Repel- lent (Wt %)	Antistat (Wt %)	Repel- lency		Charge (Kvolts)			Decay Rate (sec)		
			O	W	10% RH	25% RH	50% RH	10% RH	25% RH	50% RH
C51	None	None	0	2	5	4.3	2.2	>10	>10	>10
C52	FC-808 (0.54%)	None	6	10	5	NR	5	>10	NR	2.1
C53	None	Antistat 22 (0.56%)	0	1	5	5	5	1.1	1.3	0.15
46	FC-808 (0.51%)	Antistat 22 (0.51%)	7	10	5	5	5	.02	.03	.01
C54	None	Antistat 23 (0.55%)	0	0	5	5	5	0.01	0.04	0.01
47	FC-808 (0.53-0.64%)	Antistat 23 (0.53-0.64%)	6	10	5	5	5	0.01	0.07	0.01
C55	None	Sodium p-Toluenesulfonate (0.55%)	0	2	NR	NR	3.5	NR	NR	>10
48	FC-808 (0.51%)	Sodium p-Toluenesulfonate (0.51%)	6	10	5	5	5	1.5	2.0	0.1
C56	None	Antistat 16 (0.52%)	0	1	5	5	5	2.1	2.9	1.4
49	FC-808 (0.51-0.53%)	Antistat 16 (0.51-0.53%)	8	10	5	5	5	0.01	0.01	0.01

RH = relative humidity

NR = not run

O = oil

W = water

The results in Table 20 show that surprising and excellent antistatic and repellency properties were obtained by topically treating a nonwoven with a composition comprising an antistat and a fluorochemical repellent.

5

Example 50 and Comparative Examples C57-C59

A thermoset epoxy coating was prepared by mixing 5 grams part A (amine part) and 6 grams part B (epoxy part) of Scotchweld™ 1838-iB/A Translucent Epoxy Adhesive (available from 3M, St. Paul MN). The mixture was poured at the top of a 25.5 cm by 15.5 cm by 0.102 mm thick primed polyester terephthalate film and then drawn over the film using a No. 12 wire wound (Meyer) bar. The resulting coating was cured at 65°C for one hour in a forced air oven. The above procedure was repeated using separate 5 gram quantities of part A containing 0.33 gram 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (Antistat 10), 0.33 gram Fluorochemical Repellent FR-3, and a combination of 0.33 gram 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and 0.33 gram Fluorochemical Repellent FR-3, respectively. The cured coatings were tested for antistatic performance, oil repellency, and water repellency using Test Methods III, V, and VI. The results are shown in Table 21.

20

Table 21. Static Charge Dissipation, Oil Repellency, and Water Repellency of
Thermoset
Epoxy Coatings

Ex. No.	Repel- lent (Wt %)	Antistat (Wt %)	Repel- lency		Charge (Kvolts)	Decay Rate (sec)
			O	W	50% RH	50% RH
C5 7	None	None	1	6	5	>60
C5 8	None	Antistat 10 (2.9%)	1	3	5	24
C5 9	FR-3 (2.9%)	None	8	10	5	>60
50	FR-3 (2.9%)	Antistat 10 (2.9%)	8	10	5	9.6

RH = relative humidity

5   O = oil

W = water

The results in Table 21 show that high oil and water repellency and some
improvement in antistatic properties were obtained by using a combination of a
10   fluorochemical repellent and an ionic antistat in a thermoset epoxy coating.

Example 51 and Comparative Examples C60-C62

A moisture curable polyurethane resin was prepared by combining one
equivalent of LHT 28 (Union Carbide Corp., Danbury, CT), one equivalent of PPG
15   3025 (ARCO Chemical Co., Newtown Square, PA), and 4 equivalents of toluene
diisocyanate under a dry nitrogen purge. The mixture was heated with stirring at
80°C for 4 hours and then cooled to 60°C. A few drops of dibutyltin dilaurate was
added to the mixture, and the mixture was allowed to come to room temperature.

A thermoset polyurethane coating was prepared as follows: A portion of
20   the resulting moisture curable polyurethane resin (10 grams) was heated to about

-75-

100°C using a heat gun. About 2 ml of the heated resin was pipetted onto the top of a 25.5 cm by 15.5 cm by 0.102 mm thick primed terephthalate polyester film, and the resin was drawn over the film using a No. 12 Meyer bar. The resulting coating was cured at 65°C for 12 hours in a forced air oven and then allowed to

5   stand at ambient conditions for 10 hours. The above procedure was repeated using separate 10 gram quantities of urethane resin containing 0.157 gram 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (Antistat 10), 0.153 gram Fluorochemical Repellent FR-3, and a combination of 0.157 gram 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and 0.151 gram

10   Fluorochemical Repellent FR-3, respectively. The cured coatings were tested for antistatic performance, oil repellency, water repellency, and surface resistivity using Test Methods III, IV, V, and VI. The results are shown in Tables 22 and 23.

Table 22. Static Charge Dissipation, Oil Repellency, and Water Repellency of Thermoset Urethane Coatings.

Ex. No.	Repellent (Wt %)	Antistat (Wt %)	Repellency		Charge (Kvolts)			Decay Rate (sec)		
			O	W	10% RH	25% RH	50% RH	10% RH	25% RH	50% RH
C60	None	None	1	3	5	5	5	2.4	2.4	2.9
C61	None	Antistat 10 (1.5%)	1	3	5	5	5	0.01	0.01	0.01
C62	FR-3 (1.5%)	None	8	10	5	5	5	5.4	4.1	2.0
51	FR-3 (1.5%)	Antistat 10 (1.5%)	8	10	5	5	5	0.05	0.03	0.02

RH = relative humidity

O = oil

W = water

The results in Table 22 show that high oil and water repellency and
excellent antistatic properties were obtained when a combination of fluorochemical
repellent and ionic antistat were used in a thermoset urethane coating.

5

Table 23. Surface Resistivity of Thermoset Urethane Coatings

Example No.	Repellent (Wt %)	Antistat (Wt %)	Surface Resistivity at 26% RH and 21.7°C (ohms/square)
C60	None	None	>10E12
C61	None	Antistat 10 (1.5%)	2.67 x 10E10
C62	FR-3 (1.5%)	None	>10E12
51	FR-3 (1.5%)	Antistat 10 (1.5%)	1.75 x 10E10

RH = relative humidity

O = oil

W = water

10

. The results in Table 23 show that an improvement in antistatic properties
was obtained by using a combination of fluorochemical repellent and antistat
compound in a thermoset urethane coating.

Various modifications and alterations of this invention will become
15   apparent to those skilled in the art without departing from the scope and spirit of
this invention.

What Is Claimed Is:

     1.   A water- and oil-repellent, antistatic composition comprising (a) at least one nonpolymeric ionic salt consisting of (i) at least one cation selected from the group consisting of monovalent metal cations, divalent metal cations, and organic onium cations and (ii) at least one weakly coordinating anion, the conjugate acid of said anion having an acidity greater than or equal to that of a hydrocarbon sulfonic acid, and with the proviso that said anion is organic or fluoroorganic when said cation is a metal; (b) at least one fluorochemical repellent; and (c) at least one insulating material.

     2.   The composition of Claim 1 wherein said cation is an organic onium cation and said hydrocarbon sulfonic acid has from 1 to about 20 carbon atoms.

     3.   The composition of Claim 1 wherein said organic onium cation is a nitrogen onium cation or a phosphorus onium cation and the Hammett acidity function, H_0, of said conjugate acid is less than about -7.

     4.   The composition of Claim 1 wherein said organic onium cation is selected from the group consisting of acyclic and unsaturated cyclic organic onium cations and said anion is selected from the group consisting of organic anions and fluoroorganic anions.

     5.   The composition of Claim 1 wherein said ionic salt consists of at least one cation selected from the group consisting of alkyl phosphonium cations, aromatic nitrogen onium cations, and acyclic nitrogen onium cations; and at least one organic or fluoroorganic anion.

     6.   The composition of Claim 1 wherein said insulating material is selected from the group consisting of thermoplastic polymers and thermoset polymers.

7.   A water- and oil-repellent, antistatic composition comprising (a) at least one nonpolymeric ionic salt consisting of (i) at least one nitrogen onium or phosphorus onium cation and (ii) at least one weakly coordinating anion, the conjugate acid of said anion having an acidity greater than or equal to that of methane sulfonic acid or p-toluene sulfonic acid; (b) at least one fluorochemical repellent that is suitable for use as a melt additive; and (c) at least one thermoplastic polymer; wherein said composition is prepared by forming a melt blend of components (a), (b), and (c).

8.   A fiber comprising the composition of any of Claims 1 through 7.

9.   A fabric comprising the fiber of Claim 8.

10.   A film comprising the composition of any of Claims 1 through 7.

11.   A molded or blown article comprising the composition of any of Claims 1 through 7.

12.   A coating comprising the composition of any of Claims 1 through 7.

13.   A topical treatment composition useful in preparing a water- and oil-repellent, antistatic composition of Claim 1 comprising (a) at least one nonpolymeric ionic salt consisting of (i) at least one cation selected from the group consisting of monovalent metal cations, divalent metal cations, and organic onium cations and (ii) at least one weakly coordinating anion, the conjugate acid of said anion having an acidity greater than or equal to that of a hydrocarbon sulfonic acid, and with the proviso that said anion is organic or fluoroorganic when said cation is a metal; and (b) at least one fluorochemical repellent.

14.   A process for preparing a water- and oil-repellent, antistatic composition of Claim 1 comprising the steps of (a) combining (i) at least one

nonpolymeric ionic salt consisting of at least one cation and at least one anion, said

cation being selected from the group consisting of monovalent metal cations,

divalent metal cations, and organic onium cations, and said anion being a weakly

coordinating anion, the conjugate acid of said anion having an acidity greater than

5   or equal to that of a hydrocarbon sulfonic acid, and with the proviso that said anion

is organic or fluoroorganic when said cation is a metal, (ii) at least one

fluorochemical repellent, and (iii) at least one thermoplastic polymer; and (b) melt

processing the resulting combination.

10   15.   A process for preparing a water- and oil-repellent, antistatic

composition of Claim 1 comprising the steps of (a) combining (i) at least one

nonpolymeric ionic salt consisting of at least one cation and at least one anion, said

cation being selected from the group consisting of monovalent metal cations,

divalent metal cations, and organic onium cations, and said anion being a weakly

15   coordinating anion, the conjugate acid of said anion having an acidity greater than

or equal to that of a hydrocarbon sulfonic acid, and with the proviso that said anion

is organic or fluoroorganic when said cation is a metal, (ii) at least one

fluorochemical repellent, and (iii) at least one thermosetting polymer or ceramer or

the reactive precursors of said polymer or ceramer; and (b) allowing the resulting

20   combination to cure.

16.   A process for preparing a water- and oil-repellent, antistatic

composition of Claim 1 comprising the step of applying a topical treatment

composition to at least a portion of at least one surface of at least one insulating

25   material, said topical treatment composition comprising (a) at least one

nonpolymeric ionic salt consisting of at least one cation and at least one anion, said

cation being selected from the group consisting of monovalent metal cations,

divalent metal cations, and organic onium cations, and said anion being a weakly

coordinating anion, the conjugate acid of said anion having an acidity greater than

30   or equal to that of a hydrocarbon sulfonic acid, and with the proviso that said anion

is organic or fluoroorganic when said cation is a metal; and (b) at least one

fluorochemical repellent.

17.   A process for preparing a water- and oil-repellent, antistatic composition of Claim 1 comprising the steps of (a) dissolving (i) at least one nonpolymeric ionic salt consisting of at least one cation and at least one anion, said

5   cation being selected from the group consisting of monovalent metal cations, divalent metal cations, and organic onium cations, and said anion being a weakly coordinating anion, the conjugate acid of said anion having an acidity greater than or equal to that of a hydrocarbon sulfonic acid, and with the proviso that said anion is organic or fluoroorganic when said cation is a metal, (ii) at least one

10   fluorochemical repellent, and (iii) at least one insulating material in at least one solvent; (b) casting or coating the resulting solution on at least one substrate; and (c) allowing evaporation of said solvent.

18.   A process for preparing a water- and oil-repellent, antistatic

15   composition of Claim 1 comprising the steps of (a) combining (i) at least one nonpolymeric ionic salt consisting of at least one cation and at least one anion, said cation being selected from the group consisting of monovalent metal cations, divalent metal cations, and organic onium cations, and said anion being a weakly coordinating anion, the conjugate acid of said anion having an acidity greater than

20   or equal to that of a hydrocarbon sulfonic acid, and with the proviso that said anion is organic or fluoroorganic when said cation is a metal, (ii) at least one fluorochemical repellent, and (iii) at least one monomer; and (b) allowing polymerization of the monomer to occur.

Interr I Application No
PCT/US 00/25097

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   D06M13/46   D06M15/277   D06M15/576   D06M15/333   C09K3/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7   D06M   C11D   C09K   C07C   C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 144 367 A (LANDUCCI DENNIS P) 13 March 1979 (1979-03-13) column 1, line 59 -column 4, line 38 column 4, line 39 -column 5, line 24; claims	1,8,9, 13,16,18
A	US 5 300 357 A (GARDINER ROBERT A) 5 April 1994 (1994-04-05) cited in the application the whole document	1-18
A	US 4 666 764 A (KOBAYASHI SHIGENOBU ET AL) 19 May 1987 (1987-05-19) the whole document	1-18

☐ Further documents are listed in the continuation of box C.	☒ Patent family members are listed in annex.

° Special categories of cited documents :

'A' document defining the general state of the art which is not considered to be of particular relevance

'E' earlier document but published on or after the international filing date

'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

'O' document referring to an oral disclosure, use, exhibition or other means

'P' document published prior to the international filing date but later than the priority date claimed

'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

'&' document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 December 2000	28/12/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Koegler-Hoffmann, S

Form PCT/ISA/210 (second sheet) (July 1992)

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4144367 A	13-03-1979	AU 521901 B	06-05-1982
		AU 3588178 A	15-11-1979
		BE 866808 A	08-11-1978
		CA 1104309 A	07-07-1981
		DE 2820431 A	16-11-1978
		DK 197078 A,B,	10-11-1978
		FR 2390538 A	08-12-1978
		GB 1601839 A	04-11-1981
		JP 53139900 A	06-12-1978
		NL 7804850 A	13-11-1978
		ZA 7802606 A	25-04-1979
US 5300357 A	05-04-1994	US 5244951 A	14-09-1993
		AU 648887 B	05-05-1994
		AU 1497092 A	05-11-1992
		CA 2066012 A	03-11-1992
		DE 69221770 D	02-10-1997
		DE 69221770 T	26-02-1998
		EP 0516271 A	02-12-1992
		JP 5186907 A	27-07-1993
		KR 230711 B	15-11-1999
US 4666764 A	19-05-1987	JP 61194275 A	28-08-1986
		DE 3686500 A	01-10-1992
		DE 3686500 T	01-04-1993
		EP 0196759 A	08-10-1986